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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

General reviews of progress, reagents and methods of general application.

2455. **Analytical chemistry of fused media. 11th Annual Summer Symposium, American Chemical Society.** *Anal. Chem.*, 1958, **30** (12), 1892–1894.—Short summaries are given of the following papers presented. **Kinetics and mechanism of the dichromate - bromide reaction to yield bromine in fused nitrates,** F. R. Duke and M. L. Iverson. **Techniques for the study of metal - metal salt solutions,** S. J. Yosim. **Spectroscopy in rigid glassed solvents,** E. W. Abrahamson. **Constitution of molten salt mixtures. Mercuric bromide - alkali-metal bromides,** G. J. Janz, J. Goodkin and J. D. McIntyre. **Application of electron paramagnetic resonance methods to fused salts,** B. R. Sundheim. **Problems imposed by changes in temperature and solvent composition on the spectrophotometric analysis of fused salts,** G. P. Smith. **Electrode processes in fused salts,** J. O'M. Brockris and J. Barton. **Spectrophotometry applied to the analysis of fused salts,** D. M. Gruen. **Complexing of tantalum pentachloride by chloride ion in fused media,** C. M. Cook, jun. **Some separation processes from molten fluoride solutions,** W. R. Grimes. **Investigations of the silver - silver chloride reference electrode in the lithium chloride - potassium chloride eutectic melt,** Ling Yang and R. G. Hudson. **Fused-salt polarography using a dropping bismuth electrode,** J. J. Egan and R. J. Heus. **Reference electrodes for molten salts,** S. Senderoff, G. W. Mellors and E. R. Van Artsdalen. G. P. Cook

2456. **Purification of dithizone for determining micro amounts of metal.** A. I. Markova. *Zavod. Lab.*, 1958, **24** (9), 1069.—A quantity (1 g) of the usual dithizone reagent containing impurities such as bisphenylazothione is dissolved in 100 ml of $CHCl_3$ and shaken for 2 min. with 10 ml of 3% ascorbic acid soln. and 100 ml of dil. aq. NH_3 (1:100). The $CHCl_3$ is separated and shaken with 10 ml of the ascorbic acid soln. This operation is repeated 5 or 6 times until the ammoniacal layer no longer becomes orange. The ammoniacal extracts containing the dithizone are carefully neutralised with dil. HCl (1:1) to precipitate the dithizone, which is filtered off and washed three times with 1% ascorbic acid soln. so that the ppt. is collected in the lower part of the filter. The filter and ppt. are dried in air without heating. When dried, the fine crystals separate easily from the paper. Soln. in CCl_4, etc., are stable for 8 months at room temp. In 0·01% concn. in CCl_4 the soln. is stable at 30° for 3 months and at 40° for one month.

G. S. Smith

2457. **Rubeanic acid [dithio-oxamide] and its derivatives as colorimetric reagents. II. Dimethyl- and diethyl-rubeanic acids.** J. Xavier and Priyadaranjan Rây (Inorg. Chem. Dept., Indian Assoc. for the Cultivation of Sci., Calcutta). *J. Indian Chem. Soc.*, 1958, **35** (8), 589–594.—NN′-Dimethyl- and -diethyl-rubeanic acids react in a similar manner to rubeanic acid, giving coloured ppt. with soln. of salts of various metals such as Pd, Au and Ag. The solubilities of the metal complexes closely follow those of the rubeanates. Spot tests for Cu, Co, Ni and Pd show identification limits comparable to those of the parent compound. Spectrophotometric determinations of the metals, excluding Cu, have also been made, but in some cases the presence of excess of alkali retarded colour development.

III. NN′-Di-β-hydroxyethyl- and NN′-di*iso*-amyl-rubeanic acids. J. Xavier and Priyadaranjan Rây. *Ibid.*, 1958, **35** (9), 633–640.—The effect of substitution in rubeanic acid on its reactivity as a reagent is studied by examining the behaviour of NN′-di-β-hydroxyethyl- (**I**) and NN′-di*iso*amyl-rubeanic acid (**II**). Substitution of a H atom by an hydroxyl group in the ethyl radical increases the solubility of the product, and of its metal complexes (*e.g.*, of Cu) in certain solvents. The behaviour of **II** is like that of other disubstituted alkyl derivatives. The use of NaOH soln. of the reagents retards the colour development, as in the case of the diethyl derivative, and this effect is more pronounced with increase in the chain length of the substituent. Methods for the spectrophotometric determination of Cu (with **I**), Co and Ni (with **II**), Pd (with **I** and **II**) and Ru (with **I**) are described.

I. Jones

2458. **The application of thio salts in analysis. VI. A new and more comprehensive scheme of qualitative analysis. Analysis of the insoluble residue.** G. B. S. Salaria (Univ. of Allahabad, India). *Anal. Chim. Acta*, 1958, **19** (4), 316–319.—The original scheme (*Anal. Abstr.*, 1958, **5**, 6) is modified to provide for the possible presence of insoluble substances not previously considered. The substances now included are Ir, Rh, Ru, W, Ta, Ta_2O_5, Nb, Nb_2O_5, and the fluorides and phosphates of Sc, Y, La and other rare-earth elements.

H. N. S.

2459. **Separations involving sulphides. VI. Separation of alkaline-earth metals from some elements that form sulphides.** G. B. S. Salaria (Univ. of Allahabad, India). *Anal. Chim. Acta*, 1958, **19** (3), 244–246 (in English).—By adding 2 *N* Na_2S soln. containing mixtures of two ions, followed by addition of acid to a suitable final normality, and separation of the pptd. sulphide, it is shown that ≃ 60 mg of Ba may be separated from ≃ 20 mg of Re, Pt (6 *N* acid), Au (*N* acid) or Pd (3 *N* acid) or from ≃ 60 mg of Bi, Pb or Cd (3 *N* acid). For Au, HCl is used, for Re and Pt, HCl - ammonium acetate, and for the other metals acetic acid is used to adjust the acidity. Similar results are reported for the separation of ≃ 40 mg of Sr, 40 mg of Ca or 15 mg of Mg from Re, Pt, Au, Hg, Bi, Pd, Pb or Cd.

T. R. Andrew

2460. **Separations involving sulphides. VII. Separation of (*A*) bismuth, lead and cadmium from mercury and (*B*) bismuth and mercury from indium.** G. B. S. Salaria (Chem. Lab., Univ. of Allahabad, India). *Anal. Chim. Acta*, 1958, **19** (3), 247–248 (in English).—Binary mixtures of Bi, Pb or Cd with Hg are analysed by pptg. HgS in 6 *N* HCl with 2 *N* Na_2S and comparing the weight of the sulphide (dried at 105°) with that of the mixed sulphide obtained under less acid conditions. Mercury or Bi may be separated from In by pptn. as sulphide from *N* HCl soln.; In is subsequently pptd. from 3 *N* HCl soln. T. R. ANDREW

2461. **Eriochrome black A as an indicator for chelatometric titrations.** A. A. Abd El Raheem and Abdel-Aziz Amin (Min. of Public Health Lab., Cairo, Egypt). *Anal. Chim. Acta*, 1958, **19** (4), 327–330.—Spot tests for several metals are obtained by mixing a micro-drop of the test soln. with a micro-drop of a 1% aq. soln. of Eriochrome black A [1-(2-hydroxy-1-naphthylazo)-5-nitro-2-naphthol-4-sulphonic acid]. The colour changes from blue to pink, red or rose. The detection limits (in μg) are Zn^{2+}, 0·01; Cu^{2+}, 0·02; Pb^{2+}, 0·003; Cd^{2+}, 0·22; Mn^{2+}, 0·01; Ni^{2+}, 0·02; Co^{2+}, 0·083; Mg^{2+}, 0·54. The dye (0·1 g) is mixed with NaCl (10 g) for use as an indicator in the titration of metal ions with 0·01 *M* EDTA (disodium salt). The soln. (10 ml) are buffered with 1 ml of a soln. containing 13·5 g of NH_4Cl and 88 ml of conc. aq. NH_3 in 250 ml. The metal ions titrated are Zn^{2+}, Mn^{2+} (in the presence of a few mg of ascorbic acid to prevent pptn. of hydrated MnO_2), Ni^{2+} (at ≃ 80°), Cu^{2+} (at ≃ 80°) and Pb^{2+} (in the presence of a few mg of tartaric acid). The colour change is from red to blue. H. N. S.

2462. **New complexometric indicator of the type of Acid Chrome Dark Blue.** I. S. Mustafin, E. A. Kashkovskaya and A. N. Ivanova (N. G. Chernyshevskiĭ Saratov State Univ.). *Zavod. Lab.*, 1958, **24** (9), 1060–1061.—Acid Chrome Dark Blue 3 is more sensitive towards Mg than various other indicators of the same series. G. S. SMITH

2463. **Calculation of the titration curve, error and pH in acid - base titrations.** J. B. Schute (Lab. voor Anal. Scheikunde, Univ., Amsterdam). *Chem. Weekbl.*, 1958, **54** (8), 101–108.—The titration curve of a particular acid with a particular base can be easily deduced from two kinds of fundamental curves which are easy to memorise. The described method can also be used for the titration of a mixture of acids and bases and for finding the necessary relations for the calculation of pH. P. RENTENAAR

2464. **Acid titrants and indicators in organic solvent - water (9:1) mixtures.** A. S. Kertes and J. M. E. Goldschmidt (Hebrew Univ., Jerusalem, Israel). *Bull. Res. Council Israel, A*, 1957, **7** (1), 29–34.—Results of potentiometric titrations with *N* Na_2CO_3 of 0·1 *N* HCl, $HClO_4$ and trichloroacetic acid in organic solvents (ethanol, dioxan, acetone and others) are given and discussed in respect of the stability with time of the acid-titrants in the organic media and the applicability of the glass - calomel electrode and of various indicators in these titrations. The content of H_2O at the end of each titration was ≃ 10%. In most instances, $HClO_4$ is stable and trichloroacetic acid is unstable, with HCl behaving intermediately; stability cannot be correlated with solvent. The most satisfactory indicators are 2:4- and 2:6-dinitrophenol, Moir's indicator and Congo red. W. J. BAKER

2465. **The EDTA titration: Applications. IV.** H. Flaschka, A. J. Barnard, jun. and W. C. Broad (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Chemist Analyst*, 1958, **47** (3), 78–84.—A literature survey is presented with approx. 200 references. It includes (*i*) the determination of cations from K to Zr (and Hf), in alphabetical order, (*ii*) the indirect determination of certain anions by pptn. with a cation, the cation being then determined either in the ppt. or by back-titration of the excess, and (*iii*) the determination of certain pharmaceutical and organic compounds. These may contain metals, which can be titrated directly after suitable treatment, or anions which can be determined indirectly as in (*ii*), or they may react stoicheiometrically with metals, which are then determined in a ppt., or by back-titration of an excess. R. E. ESSERY

See also Abstracts—**2490**, Use of phenazo in determination of Mg. **2497**, Use of cadion in determination of Cd. **2575**, Use of 2-hydroxy-1-nitro-3-naphthoic acid. **2616**, S-Methylthiourea as reagent for Ni and Co.

2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

2466. **Chromatography of metal ions with filter-paper impregnated with kojic acid.** Satoru Yokota and Junko Shimada (Fac. of Sci., Kumamoto Univ.). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (9), 1144–1145.—Kojic acid (**I**) produces chelates with various metal ions, and is used for impregnating filter-paper for paper chromatography. A cotton string (5 cm) is hung from the centre of a circular filter-paper with its lower end dipping into 0·1 *M* **I**. Impurities in the paper (mainly Fe^{3+}) migrate towards the edge. The sample soln. is applied as a ring of radius 5 mm round the centre of the paper and developed with *n*-butanol - acetic acid (5 to 6 *N*, the pH is adjusted to 3·5 to 5·5 with Na acetate) (4:3, by vol.). Ferric ions migrate first, showing a grey - brown coloration, followed by Cu and Mn and Ni (the last two are not separated), which can be stained with a mixture of dimethylglyoxime (0·1 *M*) and 8-hydroxyquinoline (0·1 *M*) in ethanol. K. SAITO

2467. **Focusing ion exchange. VII. Quantitative micro-analysis of heavy metals and rare-earth elements.** E. Schumacher and H. J. Streiff (Chem. Inst., Univ., Zürich). *Helv. Chim. Acta*, 1958, **41** (6), 1771–1783.—Focusing ion exchange (*cf. Anal. Abstr.*, 1957, **4**, 2078) is extended to double focusing, *i.e.*, the formation of two stationary lines of the same metal, in the presence of two complexing agents. The relative intensity of these lines changes in proportion to the amount of chelating agent added. This phenomenon can be used for the determination of μg and ng quantities of Fe^{3+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Y^{3+} and heavy rare-earth metals. This cannot be achieved by heterogeneous ion

exchange or electrophoresis. Apparatus is described with which the phenomenon of double focusing can be used as an external indicator in the macro-titration of metal ions with a chelating agent. The end-point is determined within 0·1% of the vol. of titrant. In a variant of this procedure, a radio-isotope is added and the titration followed by the distribution of activity between the two lines. Samples containing $\geqslant 10\ \mu g$ can be titrated directly on the paper. Traces of metal ions can be determined within a few per cent. by their effect on the distribution of activity between the two lines of Co^{2+} labelled with ^{60}Co. The theoretical basis of the phenomenon is discussed. G. BURGER

2468. **Determination of copper, lead, tin and antimony by controlled-potential electrolysis. I. General method of analysis.** B. Alfonsi (Res. and Control Lab. Auto-Avio, FIAT, Turin, Italy). *Anal. Chim. Acta*, 1958, **19** (3), 276–283 (in English).—Dissolve 1 g of alloy in 10 to 12 ml of 6 *N* HCl with addition of H_2O_2. Add 40 to 50 ml of H_2O and boil for 10 to 15 min. Cool, and add a soln. of 5 g of tartaric acid. Dilute to 200 ml and add 3 g of succinic acid and 2 g of hydrazine hydrochloride. Adjust the pH to 5 with aq. NH_3 and deposit Cu at a platinum cathode potential of −0·35 V *vs.* the S.C.E. rising to −0·40 V when the current drops to 0·05 to 0·10 amp. Remove and wash the cathode, and weigh for determining Cu. Replace the copper-plated cathode for the determination of Pb. Adjust the pH to 5·4 to 5·5 and electrolyse at a cathode potential of −0·60 V *vs.* the S.C.E. After weighing the cathode, dissolve the deposit of Pb and Cu in HNO_3 and use the cathode for the determination of Sn. Add 20 ml of HCl and electrolyse at 0·8 to 1 amp. When the cathode potential reaches −0·60 V *vs.* the S.C.E. maintain it at this value. When gas evolution ceases, add 0·5 to 0·7 g of sulphamic acid, and after the current drops to 0·1 amp. add 0·2 to 0·3 g of sulphamic acid and bring the potential to −0·70 V. After weighing the cathode, strip the Sn from it with dil. (1 + 1) HNO_3 and tartaric acid, wash with H_2O, and finally with dil. (1 + 1) HCl. For Sb, heat the soln. to boiling and pass a current of 0·4 to 0·5 amp. Add KI and adjust the cathode potential to −0·45 V *vs.* the S.C.E. Continue adding KI until the soln. becomes yellow. When the current intensity remains constant remove the cathode and weigh. Recoveries have been satisfactory even in the presence of 100 mg each of Ni, Zn and Mn, 50 mg of Fe and 10 mg of Al. Silver and Bi are deposited with the Cu, larger amounts of Al inhibit deposition of Pb, and large amounts of Ni are partially co-deposited with Pb if the potential exceeds −0·65 V.

II. Application of the method to the determination of copper, lead, tin and antimony in bronzes and brasses. B. Alfonsi. *Ibid.*, 1958, **19** (4), 389–394.—The general methods described in Part I are applied to the analysis of various types of bronze and brass. T. R. ANDREW
H. N. S.

2469. **Rapid quantitative determination of copper, lead, tin, iron and zinc in copper, bronze and brass.** J. H. Maisterra (Lab. Fís. y Quím., Electrolysis del Cobre, S.A., Spain). *Chim. Anal.*, 1958, **40** (10), 385–387.—The samples are rapidly and conveniently dissolved electrolytically by preparing an anode from the material, and electrolysing with a platinum-wire cathode in HNO_3 soln. After dissolution of $\simeq$ 1 g, the sample anode is replaced by a platinum-wire anode, and the electrolysis is continued for the deposition of Cu and Pb. Tin is retained as metastannic acid on the surface of the sample electrode, and is determined after cleaning the latter with dil. aq. NH_3 before reweighing. From the soln. remaining after electrolysis, Fe and Zn are determined after pptn. as hydroxide and sulphide, respectively. J. H. WATON

2470. **Estimation of lead and bismuth, iron and manganese, and of magnesium and beryllium after paper-chromatographic separations.** I. I. M. Elbeih and M. A. Abou-Elnaga (Dept. of Chem., Univ. of Cairo, Egypt). *Chemist Analyst*, 1958, **47** (3), 59–60.—Apparatus and methods previously described (Elbeih, *cf. Anal. Abstr.*, 1957, **4**, 381; Elbeih and Amin, *Chemist Analyst*, 1956, **45**, 94; Elbeih and Abou-Elnaga, *Chemist Analyst*, 1958, **47**, 35) are applied to the ion-pairs named. Lead and Bi and Mg and Be are separated by means of the previously described phenazone and benzoylacetone - *n*-butanol systems, and Fe and Mn with 2:4:6-collidine - 0·4 *M* HNO_3 (1:1). The metals are located on indicator strips with $(NH_4)_2S$ for Pb and Bi, methanolic Na diethyldithiocarbamate for Fe and Mn, and oxine for Mg and Be, and then, with the exception of Be, dissolved from the appropriate portions of the main papers and titrated with 0·001 *M* EDTA. With Be, the spots, after being sprayed with oxine, are exposed to NH_3 while still wet, dried, and compared visually under u.v. light with a series of standard spots. For best results the original soln. should contain 1 to 10 mg of each metal per ml. Cations which do, and do not, interfere are listed for each metal. Results for known mixtures containing from 20 to 60 μg of each metal show good recoveries, with errors $\geqslant 1{\cdot}5\ \mu g$. R. E. ESSERY

2471. **The determination of trace elements in pulverised-fuel ash.** A. C. Smith (Central Electr. Authority, Res. Lab., Kingston Road, Leatherhead, Surrey). *J. Appl. Chem.*, 1958, **8** (10), 636–645.—An analysis was made of 18 samples of pulverised-fuel ash to evaluate possible recoverable metals or to give information as to its use. Since routine chemical analysis would be long and tedious, a spectrographic method was employed. Calibration graphs were based on a mixture of pure substances approximating to the composition of the ash; tin and cobalt were used as internal standards. Thirty minor constituents were determined and of these Pb, Ti, Ge and Mn were confirmed by chemical means. Average concentrations were—Ti 1%, Mn 0·1%, Cu, Pb, Zn, Ni and Cr 0·01 to 0·1%. Concn. of other elements were well below 0·01%, while Tl, Cd, Hg, Rb, W, Ag, Zr, Pt, In, Pd, La and Au were not detected. F. J. M.

2472. **Determination of trace elements in reactor materials by neutron activation analysis.** G. W. Leddicotte, W. T. Mullins, L. C. Bate and J. F. Emery. *U.S. Atomic Energy Comm.*, Rep. TID-7555, 1958, 192–215.—Comparison is made of the sensitivities of gravimetric, volumetric, colorimetric, spectrographic, mass-spectrographic and activation analysis. (13 references.)
S.C.I. ABSTR.

2473. **Use of arsenazo reagent for determining rare elements.** A. F. Kutelnikov (All-Union Inst. of Mineral Raw Materials). *Zavod. Lab.*, 1958, **24** (9), 1050–1052.—Results of a systematic study of the complexes formed by arsenazo with Zr, Ti^{4+}, Th, U^{4+}, Fe^{3+}, U^{6+}, Be, Ga, In, Sc, Al, Y, rare-earth elements, Cu, Ni and Co are described. The

optimum pH for the reaction, composition of the complex, wavelength for max. absorption, extinction coeff. and equilibrium const. are given in each case.
G. S. SMITH

2474. **Spectrographic analysis of precision alloys [Permalloy and Covar].** N. V. Buyanov and N. P. Kaminskaya (Central Sci. Res. Inst. of Ferrous Metallurgy). *Zavod. Lab.*, 1958, **24** (9), 1086–1090.—Conditions used for analysing various alloys of Ni, Mo, Mn and Si for major constituents are described.
G. S. SMITH

2475. **Gas-chromatographic separation of hydrogen isotopes D_2 and HD.** Sumio Ohkoshi, Yuzaburo Fujita and Takao Kwan (Res. Inst. for Catalysis and Chem. Dept., Hokkaido Univ., Sapporo). *Bull. Chem. Soc. Japan*, 1958, **31** (6), 770–771.—A simple gas-adsorption chromatographic apparatus capable of operating an adsorption column at any desired temp. is described. The apparatus is used for the separation of hydrogen isotopes with "molecular sieve 5A" with the column immersed in a liquid nitrogen bath.
I. JONES

2476. **Gas chromatography as a new tool for analyses of hydrogen isotopes.** Sumio Ohkoshi, Shoko Tenma, Yuzaburo Fujita and Takao Kwan (Res. Inst. for Catalysis and Chem. Dept., Hokkaido Univ., Sapporo). *Bull. Chem. Soc. Japan*, 1958, **31** (6), 772.—The gas-chromatographic techniques in which "molecular sieve 5A" is used in a liquid nitrogen bath are applied to both qual. and quant. determinations of D_2, HD and H_2.
I. JONES

2477. **Analytical control of heavy water in reactor moderator systems.** E. M. Zemyan. *U.S. Atomic Energy Comm.*, Rep. TID 7555, 1958, 175–183.—Impurities include protium oxide (H_2O), cationic impurities including radioactive nuclides, and tritium oxide. Tritium oxide may sometimes be determined by a β-counting technique in which an ion chamber is used, and D_2O is found by density or mass-spectrometric techniques; cationic impurities are concentrated by evaporation and then determined by emission spectrographic methods, and counting methods are used to estimate the concn. of radioactive nuclides; this is followed by chemical separation.
S.C.I. ABSTR.

2478. **Determination of hydrogen in lithium hydride.** K. S. Bergstresser and G. R. Waterbury (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LAMS–1698, May, 1954. Decl. Oct. 5, 1956. 39 pp.—The sample is heated with lead at 600° and the H evolved during the decomposition of the hydride is purified and oxidised to water with CuO at 400°. The analysis is completed by collecting and weighing this water. Success in development of the analytical procedure has depended on a careful design and assembly of equipment for handling samples in a dry, inert atmosphere. For seven pure hydride samples analysed by the recommended method, the estimates of the coeff. of variation varied between 0·12 and 0·41% of lithium hydride (or 1·3 and 4·2 parts per thousand) for 8 to 18 determinations on each sample. The procedure is relatively insensitive to variations in certain conditions. For single-piece samples weighing 0·2 to 0·5 g it was found to be more satisfactory than a method in which mercury is used instead of lead for sample decomposition. For powdered lithium hydride samples, the lead and mercury methods are equally satisfactory.
NUCL. SCI. ABSTR.

2479. **Determination of metallic sodium in the presence of sodium hydride.** A. E. Messner and L. B. Eddy (Callery Chem. Co., Pa.). *Anal. Chem.*, 1958, **30** (12), 1971–1972.—If metallic Na in liquid ammonia is titrated with *n*-butyl bromide in hexane, a sharp colour-change from blue to colourless is observed at the end-point. The quant. reaction—

$$2\,Na + C_4H_9Br + NH_3 \rightarrow NaBr + NaNH_2 + C_4H_{10}$$

has been applied to the determination of metallic Na in sodium hydride - mineral oil slurries. Weigh 5 ml of the slurry into a tube, add 25 ml of hexane and centrifuge. Decant the clear liquid and add 1 ml of hexane; connect the tube to the titration assembly (illustrated). Cool with liquid N, evacuate and condense 15 ml of NH_3 into the tube. Warm to b.p. and titrate under N; the titrant is standardised with metallic Na. For 9 analyses, on a sample containing 2 mg of Na per ml, the average deviation was 0·04 mg of Na per ml.
P. D. PARR-RICHARD

2480. **Use of ion-exchange resins in the analysis of rocks and minerals. Separation of sodium and potassium.** L. E. Reichen (U.S. Geol. Survey, Washington, D.C.). *Anal. Chem.*, 1958, **30** (12), 1948–1950.—Cation-exchange resins can be used to separate Na and K from other cations present in silicate rocks. An Amberlite IR-120 column, of 10 milli-equiv. capacity, is eluted with 4 *N* HCl and rinsed with H_2O to an eluate acidity of pH 5. Weigh a rock sample (< 10 cation milli-equiv.) into a platinum crucible, moisten with H_2O and add 10 ml of HF. Cover the crucible and heat it on a steam bath for 4 hr. and then evaporate the contents to dryness. Evaporate to dryness twice more with H_2SO_4 and fume off the acid. Add 0·5 ml of HCl and 25 ml of H_2O, filter if necessary and wash; adjust the final vol. to $\lessapprox 50$ ml so that the soln. is $\gtrsim 0{\cdot}1$ *N* in HCl. Pass the soln. through the resin at 2 to 4 ml per sq. cm per min. and rinse with 100 ml of H_2O. Elute Na^+ and K^+ with 850 ml of 0·12 *N* HCl at 4 ml per sq. cm per min. Determine alkalis in the eluate by weighing as chlorides, by flame photometry or by pptn.
P. D. PARR-RICHARD

2481. **Indirect complexometric titration of potassium, rubidium, caesium, thallium and ammonium.** Buddhadev Sen (Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 320–322.—The cations are pptd. with a reagent prepared as follows. Dissolve 50 g of $NaNO_2$ and 25 g of $Na_3Co(NO_2)_6$ in 150 ml of water and add, with stirring, a soln. of 2 g of $AgNO_3$ in 5 ml of water. Dilute to 200 ml, add 2 ml of acetic acid, aspirate the soln. rapidly for 5 min., keep it at 4° to 6° for 48 hr. and filter. *Procedure*—To the sample soln., containing 1 to 2 mg of the cation per ml, add an equal vol. of the reagent soln. and set aside for 2 to 3 hr. at 4° to 6°. Centrifuge the ppt. [$M_2AgCo(NO_2)_6$], wash it with ice-cold 0·5% acetic acid and dissolve it in 25 to 50 ml of water containing 0·5 ml of 5 *N* HNO_3. Adjust the pH to 7 to 8 with Na_2CO_3, add 1·5 to 2 g of NH_4SCN and an equal vol. of acetone and titrate the Co with 0·01 *M* or 0·005 *M* EDTA (disodium salt) to the discharge of the blue colour of the thiocyanate complex. When the amount of cation is 5 mg or less, the ppt. is re-dissolved in 5 ml of water with a few drops of 5 *N* HNO_3.
H. N. S.

2482. **Coulometric titration of gold with electrogenerated chloro-cuprous ion.** J. J. Lingane (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 394–401.—Details of the titration cell are given, the electrical equipment and the coulometric technique being referred to previous publications. The net titration equation is—

$$AuCl_4^- + 3\,CuCl_2^- \rightarrow Au + 3\,Cu^{2+} + 10\,Cl^-,$$

and the reaction mechanism is discussed. Quantities of Au from 1 mg to 100 mg are titrated with an average error of ±0·3%. The titration is applicable in the presence of large amounts of Cu, Ag, Hg, Pb and most of the elements commonly associated with Au. Quantities of Pt^{4+} more than half the amount of the Au cause a positive error. H. N. S.

2483. **Analytical application of 8-mercaptoquinoline (thio-oxine) and its derivatives. III. Photometric determination of small amounts of copper.** Yu. A. Bankovskiĭ and A. F. Ievin'sh (Inst. Chem., Acad. Sci., Latvian SSR, Riga). *Zhur. Anal. Khim.*, 1958, **13** (6), 643–646.—In neutral, acid and alkaline soln. thio-oxine forms with Cu^{2+} a dark-brown water-insol. salt, $Cu(C_9H_6NS)_2.0{\cdot}5H_2O$. The salt is easily extracted by chlorobenzene, bromobenzene, chloroform, amyl acetate, and *iso*-propyl alcohol. A photometric method has been developed for determining traces of Cu (3 to 30 μg) in the presence of prevalent quantities of Bi, Mn, Fe, Ni and other elements. *Procedure*—To a separating-funnel containing 15 to 20 ml of the test soln. (pH 3 to 5) add 5 ml of 10% ascorbic acid soln. followed by 10 ml of 20% KH_2PO_4 soln. (acidified with HCl to methyl orange indicator), 10 ml of saturated oxalic acid and 10 ml of conc. HCl (sp. gr. 1·18). Shake the contents of the funnel, then add dropwise, with shaking, 5 ml of reagent soln. (5 g of potassium thio-oxine dissolved in 77 ml of water and 23 ml of conc. HCl; the clear yellow soln. obtained is stable for a few weeks). After 2 to 3 min. extract the copper thio-oxinate with 10 ml of toluene or xylene. Separate and filter the extract, and measure the extinction against a blank at 431 mμ, with filter S42 or S47. W. Roubo

2484. **Rapid methods of analysis of metals and inorganic materials. VI. Colorimetric determination of copper in natural carbonate.** M. Veselý and Z. Šulcek (Centr. Geolog. Inst., Prague). *Chem. Listy*, 1958, **52** (10), 2010–2012.—The use of tetraethylthiuram disulphide (Dicupral) (disulfiram) (**I**) as a selective reagent for the detection and photometric determination of Cu (Michal and Zýka, *Anal. Abstr.*, 1955, **2**, 2040, 2345) enables Cu to be determined in the presence of a large excess of Fe if the procedure is carried out in a mixture of $HClO_4$ and H_3PO_4 after decomposing the sample with HNO_3. *Procedure*—Dissolve the sample (5 g) in a small vol. of conc. HNO_3 (the final amount of HNO_3 must not exceed 2 ml in 50 ml of the sample soln.) and transfer a 25-ml aliquot to a 100-ml flask. Cool and dilute to vol. with twice-distilled H_2O. Measure 10 ml into a 50-ml flask, add H_3PO_4 (85%) (3 ml), $HClO_4$ (70%) (1 ml), ethanol (96%) (30 ml) and about 0·01 *M* **I** (ethanolic soln.) (3 ml). Mix, cool and dilute to vol. with H_2O and measure the extinction of the yellow - brown colour at 430 mμ, and compare with a blank. The calibration curve for 0 to 30 μg of Cu must be prepared with the addition of $HClO_4$ (70%) (1 ml), H_3PO_4 (85%) (3 ml) and $Ca(NO_3)_2$ (1·6 g) in 50 ml. As little as 30 μg of Cu can be determined in the presence of 100 mg of Fe. The method is suitable for determining traces of Cu (< 0·0005%), and has an accuracy of ±1·3% (relative). The concn. of ethanol in the soln. influences the extinction and must be maintained at about 60%. Free HNO_3 affects the colour, but the addition of $HClO_4$ eliminates this interference; HCl causes high results in the presence of Fe^{3+}; in the presence of H_2SO_4, sparingly sol. $CaSO_4$ forms. J. Zýka

2485. **Analysis of copper fluoroborate electrolyte.** E. N. Lukashova, N. M. Baram and V. G. Kuznetsova. *Zavod. Lab.*, 1958, **24** (9), 1067–1068.—After electrolytic determination of Cu, the soln. is boiled with $MgSO_4$ which reacts with HBF_4 to give MgF_2, H_2SO_4 and H_3BO_3. From titrations of free H_3BO_3 in the original bath and of H_2SO_4 and total H_3BO_3 in the Cu-free hydrolysed soln., the contents of HBF_4 and H_3BO_3 in the bath are calculated. G. S. Smith

2486. **Indirect polarographic method for determination of silver.** Z. Zagórski and O. Kempiński (Lab. Anal. Central. Lab. Akumulatorów i Ogniw, Poznań, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 91–97.—The method is suitable for 0·00005 to 0·0005 *N* Ag^+ soln. and has a maximum error of 2·5%. Treat the sample with HNO_3 and evaporate to dryness on a sand bath. Dissolve the residue in water, warm, add 0·002 *N* KCl (2·5 ml) and evaporate to dryness on a water bath. Dissolve the residue in 5 ml of 0·05 *N* HNO_3 containing 0·2% of gelatin. Record the polarogram from 0 in the positive direction of the potential, or better anode - cathode polarograph from + 0·3 V; maintain the potentiometer at 2 V. Nitric acid proved to be superior to H_2SO_4 and, instead of gelatin, agar or gum arabic may be used; these do not contain Cl^-, hence there is no interference with the polarographic wave. S. Wasilewski

2487. **Potentiometric titration of a solution of silver nitrate in Divers' liquid [NH_4NO_3 - $2NH_3$] with sodium sulphide.** W. Hubicki and H. Groszek (Inst. für anorg. chem., Univ. M. Curie-Skłodowska, Lublin, Poland). *Ann. Univ. M. Curie-Skłodowska, AA*, 1956, **11** (3), 23–28 (in German).—A silver indicator electrode and a silver fluoride reference electrode are used. Results on 14 to 42 mg of $AgNO_3$ show an error of 0·5 to 1·8%. The prep. of the reagent soln. is given. T. R. Andrew

2488. **Analytical chemistry of beryllium.** E. S. Melick. *U.S. Atomic Energy Comm.*, Rep. TID 7555, 1958, 158–174.—The determination of 21 components found in beryllium and its alloys is described. Fluorimetric methods are of special value for air samples; gravimetric, volumetric and colorimetric methods are employed for the determination of Be, Al, Cr, Cu, Fe, Mg, Mn, Ni, Si, B, C, N and O, and spectrographic (arc) methods for Ag, Co, Cd, Pb, Li, Ca, Zn and Mo. (78 references.) S.C.I. Abstr.

2489. **Determination of magnesium in solution by direct photometry.** R. O. Scott and A. M. Ure (The Macaulay Inst. for Soil Res., Craigiebuckler, Aberdeen, Scotland). *Analyst*, 1958, **83**, 561–570.—The spectrographic determination of Mg in soln. by the porous cup - spark method has been greatly facilitated by use of the direct-reading instrument described, which is attached to a Hilger small quartz spectrograph. The Mg line at 2802 A is used with the Sr line at 4077 A as internal standard. Applications to soil extracts, plant ash and

other materials are described. Soln. containing from 0·3 to 24 p.p.m. of Mg are analysed directly with a coeff. of variation of $\simeq \pm 2\%$. Interference by other elements is negligible with most types of agricultural sample. A. O. JONES

2490. **Photometric determination of magnesium with phenazo.** V. I. Kuznetsov, L. M. Budanova and L. A. Nenasheva (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR). *Zavod. Lab.*, 1958, **24** (9), 1053–1056.—Phenazo [3:3′ - dinitro - 4:4′ - bis - (*p* - hydroxyphenylazo)-diphenyl], a dark-brown powder, insol. in water and acids, gives yellow soln. in ethanol, acetone, $CHCl_3$ and benzene, and red soln. in alkalis, and is adsorbed by $Mg(OH)_2$ showing a colour change to bluish violet. For the determination of Mg it is preferable to Titan yellow since its soln. are more stable, the alkalinity is not so critical, the presence of 10% of H_2O_2 or 15% of NaClO can be tolerated, there is no interference by Ti (2000-fold) and that of carbonates and silicates is much reduced, and it is twice as sensitive. For the determination of Mg in alloys of Ti, the sample (1 g) is dissolved in 70 ml of conc. HCl and an aliquot (10 ml) of the diluted soln. (250 ml) is diluted to 50 ml and mixed first with 1·5 ml of 30% H_2O_2, 10 ml of a 0·5% soln. of gelatin stabilised by phenol, and 5 ml of a 0·005% soln. of phenazo in ethanol or in 0·1 *N* NaOH, then with 20 ml of 20% NaOH soln., and finally diluted to 100 ml. The extinction can be measured at once or within 1 hr. at 560 to 580 mμ. The calibration curve is obtained by use of a soln. prepared by dissolving 0·25 g of Mg in 10 ml of HCl and diluting to one litre. The method was checked with excellent results over the range 0·025 to 0·7%. For the determination of Mg in alloys of Al, the sample (0·2 g) is treated with 20 ml of 20% NaOH soln., the soln. is diluted to between 120 and 150 ml, and the insol. matter is filtered off and washed with 2% NaOH soln. and then dissolved in 10 ml of conc. HCl. After addition of NaOH soln. until a bluish-violet colour is obtained with Congo red paper, 16 ml of a 5% soln. of Na diethyldithiocarbamate is added and the soln. is diluted to 100 ml. Alternatively, in alloys containing $< 0{\cdot}5\%$ of Mn and no Ni, 15 ml of a borate buffer soln. (pH 9·5 to 9·6) can be added instead of the carbamate. A portion (5 or 10 ml) of the filtered soln. is diluted to about 50 ml, treated with 5 ml of 0·5% gelatin soln. and 10 ml of 0·005% phenazo soln., followed by 15 ml of 20% NaOH soln., then diluted to 100 ml and the extinction measured. The method is suitable for duralumin, high-silicon alloys, etc.
G. S. SMITH

2491. **Determination of magnesium content of calcium phosphates and commercial lime.** D. E. Jordan and C. F. Callis (Chem. Dept., Univ. of Colorado, Boulder). *Anal. Chem.*, 1958, **30** (12), 1991–1993.—After removal of Fe^{3+}, Mn^{3+} and Al^{3+} as basic acetates, Mg^{2+} are pptd. with 8-hydroxyquinoline in the presence of Ca oxalate. By substituting Na^+ for NH_4^+ in the reagents, pptn. of magnesium ammonium phosphate is avoided. The 8-hydroxyquinoline pptd. by Mg^{2+} is liberated and titrated amperometrically with BrO_3^- - Br^- reagent. For Mg^{2+} added to calcium phosphate, the standard deviation was $< \pm 2\%$ (8 analyses).
P. D. PARR-RICHARD

2492. **Colorimetric determination of magnesium in silicates.** W. Bodenheimer and M. Gaon (Geolog. Survey of Israel, Jerusalem). *Bull. Res. Council Israel, A*, 1958, **7** (3), 117–120.—The pptn. as magnesium ammonium phosphate is carried out by using a soln. of NaCl (20 g), NH_4Cl (20 g), diammonium oxalate (12 g), $(NH_4)_2HPO_4$ (2 g) and water (1 litre). The ppt. is filtered off and washed with aq. NH_3 (1:3). A blank is carried out. Phosphoric oxide is then determined colorimetrically by dissolving the ppt. in dil. HNO_3 (50 ml) and treating the soln. with 10 ml of ammonium vanadate soln. [1·25 g in HNO_3 (1:1) (400 ml) plus ammonium molybdate (50 g) in water (450 ml) made up to 1 litre]. The colour is measured at 410 to 460 mμ. As little as 50 μg of MgO can be determined by this method.
C. A. SLATER

2493. **Flame-photometric determination of strontium in the presence of calcium, barium, magnesium and yttrium in soil extracts and plant ash for agricultural purposes.** H. Kick (Agric. Chem. Ind., Univ. Bonn, Germany). *Z. anal. Chem.*, 1958, **163** (4), 252–262.—Factors influencing the intensity of the Sr lines and bands are discussed. Large amounts of Ba are separated as barium chromate from a soln. of the sample at pH 4·5 with ammonium dichromate in the presence of ammonium acetate. Strontium and Ca are pptd. from the filtrate as oxalates, at pH 3·8 to 4·3, thus eliminating interference from Al, Fe, Mg and PO_4^{3-}. The ppt. is dissolved in HCl, and the emission due to Ca is measured at 422·7 mμ and that due to Sr at 460·7 mμ in an acetylene - air flame. Any Y present in this soln. is measured at 467·4 mμ, but this element can usually be disregarded. A correction is made for Ca from a calibration curve. B. B. BAUMINGER

2494. **The solvent extraction of zinc with dithizone.** G. K. Schweitzer and C. B. Honaker (Dept. of Chem., Univ. of Tenn., Knoxville, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 224–228 (in English).—The extraction of zinc into organic solutions of dithizone has been studied. The effects of several organic solvents ($CHCl_3$, CCl_4, benzene, chlorobenzene and dichloromethane) and anions are reported. T. R. ANDREW

2495. **Precipitation of zinc sulphide by the hydrolysis of thioacetamide.** R. B. Hahn and F. M. Shellington (Wayne State Univ., Detroit, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 234–238 (in English).—In an attempt to reduce contamination by Co, conditions for the pptn. of Zn with thioacetamide were studied. Coarse ppt. were obtained, but were seriously contaminated with CoS (2 to 20% of Co). Best results were obtained by pptn. with H_2S under pressure in the presence of sulphate - bisulphate buffer (100 g of $Na_2SO_4.10H_2O$ in 900 m of H_2O plus 13% $NaHSO_4.H_2O$ soln. to pH 2) and 20% NH_4SCN soln. Under these conditions, the amount of Co co-pptd. after 1 to 2 hr. was no more than 0·5% of that present. T. R. ANDREW

2496. **Polarographic determination of very small amounts of zinc in ferromanganese and in manganese ores containing cobalt.** S. Král and B. Kysil (Spojené Ocelárny, Kladno, Czechoslovakia). *Hutn. Listy*, 1958, **13** (8), 716–717.—*Procedure*—Into each of two iron crucibles place 2 g of the finely powdered sample, and add 4 mg of pure zinc to one as a standard. Fuse with Na_2O_2 (6 g), cool, place each crucible with the melted sample in a nickel vessel, cover with H_2O (250 ml) and heat for 10 min. Cool, remove the iron crucible, transfer the soln. to a 500-ml flask, mix and filter. Zinc passes into the filtrate as Na_2ZnO_2, whilst Co, Ni, Cu, Mn and Fe

remain in the ppt. To 250 ml of the filtrate add conc. HCl and heat until the vol. is 50 ml. Transfer to a 200-ml flask, add satd. NH_4Cl soln. (20 ml), conc. aq. NH_3 (50 ml), satd. Na_2SO_3 soln. (10 ml) and gelatin soln. (1%) (11 ml). Dilute to vol., transfer to a polarographic vessel and record the wave from 0 V. J. ZÝKA

2497. **Use of "cadion" in analytical chemistry. I. Spectrophotometric micro-determination of cadmium.** P. Chavanne and C. Geronimi. *Anal. Chim. Acta*, 1958, **19** (4), 377–388 (in French).—Cadion (*p*-nitrophenyldiazoaminoazobenzene) exhibits an absorption max. at 560 mμ under the experimental conditions described. Absorption at this wavelength diminishes in the presence of increasing concn. of Cd^{2+}. The reagent soln. is prepared by mixing 10 ml of cadion soln. (0·02% in 0·02 *N* ethanolic KOH), 25 ml of 2 *N* KOH, 50 ml of ethanol (95%), 5 ml of K Na tartrate soln. (20%) and 1 ml of poly(vinylpyrrolidone) soln. (25%), and diluting to 100 ml. *Procedure*—Add the neutral, faintly acid or faintly ammoniacal soln. of Cd^{2+} to 10 ml of the reagent soln. Determine the difference between the extinction at 560 mμ of this soln. and that of one containing no Cd, in 1-cm cells, and prepare a calibration graph in the same manner. The useful range is 0·05 to 0·5 p.p.m. of Cd in the final soln. The ratio of organic ligand to Cd in the complex is 3:1. Of 18 common anions, only CN^- interfere. Among 19 common cations tested, only NH_4^+, Na^+, Li^+, Zn^{2+}, Pb^{2+}, Bi^{3+}, Al^{3+} and Sb^{3+} are without disturbing effect. Methods for the elimination of interference are described. H. N. S.

2498. **Estimation of mercuric salts by reduction with sodium formate.** Sameer Bose (Chem. Dept., Mahakoshal Mahavidyalay, Jabalpur). *J. Indian Chem. Soc.*, 1958, **35** (9), 641–644.—A procedure is described for evaluating mercuric salts by reduction to metallic Hg with a 40% soln. of Na formate; the error is ≯ 1%. With slight modification the method can be used for volumetric determinations with thiocyanate soln. Neutral or acid soln. of various salts of Hg were successfully analysed, except mercuric cyanide which was not reduced. Silver and Pb do not interfere. I. JONES

2499. **Colorimetric determination of boron with Victoria violet.** C. A. Reynolds (Kansas Univ., Lawrence, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. AECU-3845, 1958. 12 pp.—In the pH range of 7·7 to 10·0, the absorbance of the dye, Victoria violet, is markedly lowered by the presence of boric acid. A simple colorimetric method for B in the range of 0·02 to 0·60 mg was based on this decrease in the absorbance. Measurements were made at 540 mμ on soln. adjusted to pH 8·75. NUCL. SCI. ABSTR.

2500. **Determination of boron in boron carbide - zirconium clad with Zircaloy.** V. F. Consalvo (Knolls Atomic Power Lab., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KAPL-M-VFC-5, Oct. 2, 1958. 8 pp.—A method is described for the determination of > 10 mg of B in boron carbide - zirconium material clad with Zircaloy. The sample is refluxed in quartz ware with conc. HCl - 5% HF. The acid-insol. residue is filtered off, ashed and fused with Na_2CO_3. The melt is dissolved in HCl and adjusted with NaOH to precipitate any hydrolysable elements which may interfere with the final boron titration. The B in the HCl - HF filtrate is separated from the bulk of the zirconium with a $BaCO_3$ pptn. The acid-insol. and acid-sol. B are then determined individually by a potentiometric mannitol titration. NUCL. SCI. ABSTR.

2501. **Estimation of boron-10 burn-up by flame-photometric lithium determination.** D. Dutina (Knolls Atomic Power Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2006–2008.—In the method described, the burn-up is measured by determining flame-photometrically the lithium produced by means of the $^{10}B\ (n,\alpha) \rightarrow {}^7Li$ reaction. A pptn. with aq. NH_3 reduces the radioactivity hazard. The over-all accuracy of the procedure is about 5%. K. A. PROCTOR

2502. **Determination of aluminium in true solution in the presence of colloidal hydrated alumina.** Katsumi Goto, Hiroshi Ochi and Takeshi Okura (Faculty of Engng, Hokkaido Univ., Sapporo). *Bull. Chem. Soc. Japan*, 1958, **31** (6), 783–784.—If, in the usual chloroform extraction of Al as the 8-hydroxyquinolinate, the shaking of the extraction mixture (at pH 4·5 to 9·5) is limited to 10 sec., at 20°, then only the Al in true soln. is extracted. To determine total Al, colloidal Al is decomposed by boiling with HCl before the extraction. I. JONES

2503. **The polarographic determination of aluminium. V. The oscillographic polarography of aluminium in calcium chloride solution.** G. F. Reynolds and T. J. Webber (Chem. Inspectorate, Min. of Supply, Kidbrooke, London). *Anal. Chim. Acta*, 1958, **19** (3), 293–298 (in English).—Conditions have been established for the direct polarographic determination of Al on the Randles cathode-ray polarograph (*cf. Analyst*, 1953, **78**, 314), in the range 0·5 to 100 μg of Al per ml. Stable polarograms were obtained at $CaCl_2$ concn. below 0·3 *M* and at pH 3·9 to 4·2. The value of the start potential is critical and is a function of pH and concn. of Al. A buffer concn. of 10^{-3} *M* K H phthalate is desirable in the basal soln. Good results, free from threshold effects, are reported for 50 and 100 μg of Al per ml on conventional instruments. T. R. ANDREW

2504. **Coulometric titration of aluminium.** R. T. Iwamoto (Dept. of Chem., Univ. of Kansas, Lawrence, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 272–276 (in English).—The H^+ liberated on chelation of Al with 8-hydroxyquinoline are titrated with electrolytically generated OH^-. Two basal soln. were employed—(*a*) 59% v/v ethanol saturated with Na_2SO_4 and 0·0048 *M* in 8-hydroxyquinoline for 56 and 5·6 μg of Al; (*b*) 48% v/v ethanol 0·049 *M* in Na_2SO_4 and 0·0061 *M* in 8-hydroxyquinoline for 560 μg of Al. The aluminium soln. was added to the basal soln. (20 ml for 5·6 μg of Al, 75 ml for 56 μg of Al, 75 ml plus 0·5 ml of satd. KCl soln. for 560 μg of Al) and N was passed through the soln. to free it from dissolved CO_2. The progress of the titration was followed with a pH meter. For 560 μg of Al the error ranged from −2 to + 4 μg (10 determinations), for 56 μg of Al from −0·6 to + 1·0 μg (6 determinations) and for 5·6 μg of Al from −0·03 to −0·46 μg (5 determinations). T. R. ANDREW

2505. **Spectrophotometric determination of microgram quantities of indium.** J. E. Johnson, M. C. Lavine and A. J. Rosenberg (Lincoln Lab., M.I.T.,

Lexington, Mass.). *Anal. Chem.*, 1958, **30** (12), 2055–2056.—When 5:7-dibromo-8-hydroxyquinoline (**I**) reacts with 0 to 100 μg of In, Beer's law is strictly obeyed. Neutral salts inhibit the rate of colour formation, but do not interfere. Add 2·5 ml of 0·2 *M* K H phthalate to the sample in a stoppered tube, adjust the pH to between 3·5 and 4·5 and dilute to 10 ml with H_2O. Add 5 ml of **I** (0·1% in $CHCl_3$), stopper the tube and shake for 5 min., which is long enough to overcome the salt effect. Measure the extinction of the $CHCl_3$ layer at 415 mμ, with $CHCl_3$ as a reference soln. Up to 400 μg of As^V, As^{III}, Pb, Zn or Ce can be tolerated, but Sn^{II}, Sb^{II}, Fe^{III}, Al^{III} and Cu^{II} interfere.
P. D. PARR-RICHARD

2506. **Analysis of indium antimonide and arsenide and gallium arsenide.** Yu. A. Chernikhov and T. V. Cherkashina (State Sci. Res. Inst. of Rare Metals). *Zavod. Lab.*, 1958, **24** (9), 1057–1058.—The method is based on titration with bromate, potentiometrically or visually with methyl red as indicator, of antimony or arsenic in the soln. of the alloy in conc. H_2SO_4 and $(NH_4)_2SO_4$. G. S. SMITH

2507. **The spectrographic analysis of indium, thallium and gallium.** N. Krasnobaeva. *Khim. i Ind., Sofia*, 1958, **30** (1), 16–17.—The intense background that hinders the determination of these elements when graphite electrodes are used can be reduced by the addition to the sample of a mixture of K_2SO_4 and ZnS (1:1) in a weight equal to that of the sample. ABSTR. BULG. SCI. LIT.

2508. **Co-precipitation of thallium with cadmium sulphide.** G. V. Efremov and I. Yu. Andreeva. *Vestn. Leningr. Univ.*, 1958, No. 10, *Ser. Fiz. i Khim.*, (2), 117–121.—The use of CdS as a collector for microgram amounts of Tl is studied. The optimum pH of the soln. containing Cd and Tl for pptn. with H_2S at 70° to 80° is between 5 and 5·6. The soln. is set aside for 16 to 17 hr. before filtration. Complete pptn. of Tl does not occur even when the ratio of Cd to Tl is 200:1. By addition of a further amount of Cd to the filtrate and re-pptn. with H_2S, and repeating the process three or four times, the separation can be made almost complete. Separations nearly as complete as those with H_2S can be obtained by the addition of CdS to the soln. of Tl. G. S. SMITH

2509. **Colorimetric determination of thallium with methyl violet.** G. V. Efremov and Chzhi-Gu Syul. *Vestn. Leningr. Univ.*, 1958, No. 16, *Ser. Fiz. i Khim.*, (3), 156–159.—Various proposed procedures for the preliminary treatment of samples in the colorimetric determination of Tl with methyl violet are tested by using ^{204}Tl. The sample is best decomposed by acid treatment, the soln. then being evaporated to dryness on the water bath; higher temp. lead to losses of Tl. The separation of Tl from Sb by pptn. of SbOCl is not recommended since, with a small content of Tl, up to 60% is co-pptd. with the Sb. For the oxidation of Tl^+, the use of chlorine or bromine water gives best results; the use of $NaNO_3$ is not recommended. The ions I^- and SCN^- interfere in the determination, but VO_3^- and MoO_4^{2-} do not, since their compounds float at the boundary layer between the aq. and organic phases. (*Cf.* Kovařík and Moučka, *Anal. Abstr.*, 1957, **4**, 3263.) C. D. KOPKIN

2510. **Hypophosphorous acid as a gravimetric reagent for scandium.** D. R. Bomberger (Univ. Calif. Radiation Lab., Livermore, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1907–1908.—Hypophosphorous acid compares favourably with eight other reagents mentioned. *Procedure*—Dissolve a sample (containing 5 to 50 mg of Sc) in 2 ml of warm conc. HCl and dilute to 25 ml with H_2O. Heat nearly to boiling, add 2 ml of H_3PO_2 (30 to 32%) dropwise with stirring and digest for 1 hr. on a steam bath. When cold, decant through a fine sintered crucible, transfer and wash the ppt. first with 2% H_3PO_2, then with a little H_2O, and finally with ethanol. Dry at 110° before weighing. Other acids of P and oxidising agents interfere and a list of interfering elements is given. P. D. PARR-RICHARD

2511. **Determination of metal ions by hexa-amminocobalt chloride and sodium fluoride. IV. Indirect colorimetric determination of scandium.** Tôru Nozaki and Yoshimasa Takashima (Fac. of Engng, Ehime Univ., Niihama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (9), 1024–1026.—Scandium (< 0·8 mg) is quant. pptd. with $Co(NH_3)_6Cl_3$ (**I**) and NaF at pH 3 to 4 (Takashima, *Anal. Abstr.*, 1959, **6**, 84). The ppt. is dissolved in aq. NH_3 and the Co is determined colorimetrically with nitroso-R salt. The sample soln. (5 ml for < 0·1 mg of Sc, 1 to 2·5 ml for more) is mixed with NaF soln. (3%, 0·5 ml), made pH 3 (bromophenol blue), treated with **I** (0·05 *M*) until the soln. becomes faintly orange and after 3 hr. filtered with a filter-stick with pulp. The ppt. is washed with water and dissolved in warm aq. NH_3. When the pulp is coloured, it is warmed with HNO_3 (1 + 1, one drop) and water and filtered with the same stick. The filtrate is combined with the ammoniacal soln., and evaporated to dryness with saturated Na_2S soln. (a few drops). The residue is dissolved in conc. HNO_3 (a few drops) and submitted to colorimetry with nitroso-R salt. K. SAITO

2512. **Separation of scandium from lanthanide elements with ion-exchange resin.** Jun Yoshimura, Yoshimasa Takashima and Hirohiko Waki (Fac. of Sci., Kyushu Univ., Hakozaki, Fukuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (10), 1169–1172.—The separation of Sc from Y and lanthanide elements (*cf.* Kraus, *J. Phys. Chem.*, 1954, **58**, 11) is improved by the use of 13·3 *N* HCl. The mixture containing Sc (< 3 mg of Sc_2O_3) and lanthanide elements (< 20 mg) in 13·3 *N* HCl (3 ml) is passed through a column of Dowex 1-X8 (Cl) (50 to 100 mesh) (wet vol. 30 ml), which is then eluted with 13·3 *N* HCl; lanthanide elements are collected in the first 25-ml portion. The column is then eluted with 6 *N* HCl; Sc is collected in the first 60-ml portion. The separation can also be carried out with Dowex 50-X12 (100 to 200 mesh), Sc (< 1·5 mg of Sc_2O_3) then being eluted with ammonium acetate buffer (0·5 *M*) (pH 4·6) (< 50 ml), and lanthanide elements with *M* ammonium acetate buffer (pH 5·0). K. SAITO

2513. **Determination of metals with standard potassium ferrocyanide solution. XII. Determination of lanthanum.** Yoshio Fujita (Fac. of Engng, Osaka Univ., Miyakojima-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (10), 1256–1259.—The reaction between La^{3+} and $Fe(CN)_6^{4-}$ was examined potentiometrically for 2 to 33 mg of La per 50 ml. The titration (1 drop per 25 sec.) is carried out at pH 5·8 to 6·6 in the presence of 20 to 30% ethanol, at 10° to 25°, 0·1 *N* iodine (0·02 ml) and 0·2% starch soln. (1 ml) being used as indicator. K. SAITO

2514. **Chemical analysis of iron, nickel, aluminium, silicon and calcium in dysprosium metal** R. F. Dufour (Knolls Atomic Power Lab., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KAPL-M-RFD-1, Aug. 1, 1958. 9 pp.—The determinations of Fe, Ni, Al, Si and Ca present as impurities in dysprosium metal were performed by routine methods and without deviation from standard procedures. Colorimetric methods were used in determining Fe, Ni, Al and Si, while Ca was determined flame-photometrically. The standard addition technique was used for all analyses and, when possible, separations were made in order to check the effects of dysprosium.

NUCL. SCI. ABSTR.

2515. **Dissolution of rare-earth oxides in pyrophosphoric acid.** S. S. Moosath and K. N. N. Kurup (Univ. of Kerala, Trivandrum, India). *Chem. & Ind.*, 1958, (41), 1321–1322.—To enable satisfactory spectrophotometric determinations of rare-earth elements to be made, the sample (CeO_2, La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, or a mixture thereof) can be dissolved by heating with pyrophosphoric acid (10 ml) at $\simeq 200°$ for 20 min., cooling the gel, adding H_2O and mixing well until a clear colourless soln. is obtained. The soln., which becomes slightly turbid after 24 hr., can be diluted if necessary. The max. absorption wavelength and the extinction coeff. are unaffected in pyrophosphoric acid soln. This procedure is especially useful when the sample contains much CeO_2. W. J. BAKER

2516. **Quantitative separation of small amounts of rare-earth elements from thorium, uranium and zirconium by ion exchange.** H. J. Hettel and V. A. Fassel (Ames Lab., Iowa, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. ISC-851, Dec., 1956, 71 pp.—A successful method has been developed for the determination of certain rare-earth elements in thorium in the fractional p.p.m. range. The procedure is based on the ion-exchange chromatographic separation of rare-earth elements plus added yttrium carrier from the thorium, followed by emission spectrographic determination of the rare-earth-element impurities in the yttrium carrier. A simultaneous separation from rare-earth elements of the common-element impurities present in the thorium has been accomplished. A high degree of compensation for procedural errors is achieved by the use of a pure rare-earth element as both the carrier in the separation and purification procedure and the matrix material in the spectrographic determination. The method fulfils the requirements of accuracy, sensitivity and speed necessary for use in the routine analysis of reactor-grade thorium metal. It can also find application, in its present form, for the simultaneous determination of parts per 10^9 of common-element impurities in thorium. NUCL. SCI. ABSTR.

2517. **Analysis of reactor-grade graphite.** H. G. MacPherson. *U.S. Atomic Energy Comm.*, Rep. TID 7555, 1958, 184–191.—Sampling, processing and analytical techniques are outlined and comparative tests for the determination of B are given.

S.C.I. ABSTR.

2518. **o-Diketone dioximes and their metal complexes. VIII. Photo-electric determination of the cyanide ion with palladium α-furil dioximate.** Kenichiro Yamasaki and Ryojiro Ito (Kita College, Osaka Univ., Toyonaka, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (8), 914–916.—Brooke's Pd α-furil dioximate (**I**) method for the detection of CN^- (*Anal. Chem.*, 1952, **24**, 583) was modified for the photometric determination of CN^-. α-Furil dioxime, liberated by the reaction of **I** with CN^- in an ammoniacal soln. of pH $\simeq$ 10, is treated with Ni^{3+} and gelatin (protective colloid); the extinction at 480 mμ is proportional to the concn. of CN^- for 2 to 5 μg per ml, and remains unchanged for 3 hr. Interfering ions are removed with the cation-exchange resin, Amberlite 100, or masked by the addition of a masking agent, *e.g.*, tartaric acid. The sample soln. (45 ml) is mixed with the reagent (40 mg of **I** per 25 ml of 6 *N* aq. NH_3 soln.) (1 ml), NH_4Cl soln. (5%) (0·5 ml), $NiSO_4$ soln. (0·5%) (0·2 ml) and gelatin soln. (0·5%) (1 ml) and made up to 50 ml, and the extinction is measured at 480 mμ. K. SAITO

2519. **Bromatometric analyses. V. Determination of thiocyanate.** E. Sugár and L. Szekeres (Agric. Chem. Inst., Univ. Budapest, Hungary). *Z. anal. Chem.*, 1958, **163** (6), 401–402.—A dil. soln. of SCN^- can be titrated accurately with 0·1 *N* $KBrO_3$ in *N* HCl soln., with iodised starch soln. as indicator. B. B. BAUMINGER

2520. **Effect of selected organic compounds on the determination of silica by the molybdenum blue method.** E. Richardson (Dept. of Chemistry, Whitehaven Coll. of Further Education, Cumberland, England). *Analyst*, 1958, **83**, 586–588.—The effects of a number of organic compounds on the determination of SiO_2 by the molybdenum blue method were classified into five groups. The first group produced a small additive effect on the amount of SiO_2 determined and included many of the sugars with a reducing group, *e.g.*, rhamnose, sorbose, mannose, L-arabinose and xylose. Up to 200 mg of any of these in a soln. containing only 0·1 mg of SiO_2 caused an error of $<4\%$. Fructose, the only member of the second group, produced an additive effect followed by a decrease in the amount of SiO_2 determined. The third group, which included glycine and *n*-butyric acid, produced a depressive effect increasing with the amount added until a ppt. was formed. The fourth group produced no effect until a certain amount of material was present, after which the amount of SiO_2 found decreased rapidly with further additions. This group included mannitol, dulcitol, sorbitol, erythritol and gluconic acid. The fifth group consisted of a number of compounds that had no effect on the determination. These (with the limiting amounts investigated) were sucrose (2 g), inositol (500 mg), ethanediol (1 ml), succinic acid (500 mg), arabonic acid (400 mg), galactonic acid (400 mg), glutamic acid (300 mg) and glucuronic acid (200 mg).

A. O. JONES

2521. **Effect of trichloroacetic acid on determination of silicate and phosphate with molybdate reagent.** E. S. Dellamonica, E. W. Bingham and C. A. Zittle (Eastern Regional Res. Lab., Eastern Utilization Res. and Development Div., U.S. Dept. of Agric., Philadelphia, Pa.). *Anal. Chem.*, 1958, **30** (12), 1986–1988.—The strongly acid molybdate reagent for PO_4^{3-} also gives some colour with silicate, which is greatly enhanced (× 4) when trichloroacetic acid (**I**) is present and can lead to large errors in the determination. To a lesser degree (by 26%) **I** also enhances the silicate colour obtained with the low-acidity molybdate reagent for SiO_2; the colour thus formed is independent

of the H_2SO_4 concn. and is not influenced by the vol. to which the reagent is added. The effect may be useful analytically. P. D. PARR-RICHARD

2522. **Use of perchloric acid for the determination of silica in aluminosilicates.** Z. Marczenko and A. Stępień (Zaklad Anal. Inst. Chem. Ogólnej, Warszawa, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 169–171.—Experiments were carried out for the determination of SiO_2 in aluminosilicates by evaporating the sample with HCl, $HClO_4$ or H_2SO_4. The use of $HClO_4$ gave the quickest and most accurate results. Experimental details are discussed. S. WASILEWSKI

2523. **Proton activation analysis in the determination of submicrogram amounts of boron in silicon.** R. A. Gill (A.E.R.E., Harwell, England). A.E.R.E. Report C/R 2758, 1958, 50 pp.—Possible nuclear reactions between protons and light elements are considered. The present method depends on the reaction $^{11}B(p,n) \rightarrow {}^{11}C$ and the reaction $^{30}Si(p,n) \rightarrow {}^{30}P$ is used to monitor the proton flux. The samples (> 1 g) were cut with flat surfaces to the dimensions 3 mm × 3 mm × 40 mm or with two flat surfaces at right angles. After being etched in NaOH soln. the silicon was wrapped in tantalum foil (0·002 in. thick) and bombarded with protons (max. energy 20 MeV) for between 20 and 150 min. The sample was then etched in a soln. containing HNO_3 and HF and the γ-activity due to ^{30}P was recorded under standard conditions. The ^{11}C in samples with high contents of B was then recorded in a well-type sodium iodide γ-counter and the content of B was deduced from the ^{30}P and ^{11}C activities. For samples with low contents of B, the ^{11}C was separated chemically before being counted. The method is suitable for the analysis of silicon with contents of B down to 0·003 p.p.m. G. J. HUNTER

2524. **Photometric determination of germanium with 9-[*p*-(N-dimethylamino)]phenyl-2:3:7-trihydroxy-6-fluorone.** N. F. Kazarinova and N. L. Vasilieva (Inst. Chem. Ural Branch of Acad. Sci. USSR, Sverdlovsk). *Zhur. Anal. Khim.*, 1958, **13** (6), 677–681.—Adjust the test soln. (in HCl) so that it is 0·75 to 1 *N* with respect to HCl. For concn. of Ge > 10 μg (as GeO_2) take an 8-ml aliquot, and, for higher concn., a smaller aliquot which must be diluted to exactly 8 ml with 0·9 *N* HCl. Add 2 ml of a 0·05% soln. of the reagent and set aside in the dark for 1 hr. Measure the extinction of the soln. in a 10-mm cell, with green filters, against a blank which should contain all the elements in the sample except Ge, and calculate the germanium content from a calibration graph. It is important when preparing a calibration curve that the same temperature conditions are maintained. The advantage of 9-[*p*-(N-dimethylamino)]phenyl-2:3:7-trihydroxyfluorone over phenylfluorone is that the soln. of its germanium compounds are stable in acid media at concn. up to 1·2 μg of GeO_2 in 1 ml. W. ROUBO

2525. **The use of naphthalene derivatives in inorganic analysis. VI. A new reagent for the fluorimetric detection of tin.** J. R. A. Anderson, J. L. Garnett and L. C. Lock (N.S.W. Univ. of Technol., Sydney, Australia). *Anal. Chim. Acta*, 1958, **19** (3), 256–259 (in English).—Bivalent tin gives an intense blue fluorescence with 6-nitro-2-naphthol-8-sulphonic acid under u.v. irradiation. The spot, on paper, should be sprayed with 15 *N* aq. NH_3 before examination. Of 55 ions studied, only Sn^{2+} showed strong fluorescence. Small amounts (10^{-12} to 10^{-7} g) showed only faint fluorescence. T. R. ANDREW

2526. **Luminescence method of control of alkaline tinning baths.** K. F. Gudymenko, M. U. Belyĭ and M. A. Skachko (T. G. Shevchenko Kiev State Univ.). *Zavod. Lab.*, 1958, **24** (9), 1066–1067.—The method is based on the fact that Sn^{2+} in conc. H_2SO_4 show luminescence when excited by u.v. radiation of 200 to 250 mμ. No effect is produced by Sn^{4+}. The sensitivity is 0·1 g of Sn^{2+} per litre. A sample from the bath is mixed with 50 times its vol. of conc. H_2SO_4 and examined in a quartz cell. An automatic method of indicating when the content of Sn^{2+} exceeds a certain value is described. G. S. SMITH

2527. **Dialkyl and diaryl phosphorodithioates as analytical reagents. VII. Amperometric and visual titration of lead with nickel diethyl phosphorodithioate in the presence of barium, calcium, zinc and other elements.** A. I. Busev and M. I. Ivanyutin (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (6), 647–651.—*Amperometric titration*—The soln. to be analysed should contain 0·005 to 0·03 g of Pb and may contain up to 0·25 g of Ba, Sr, Ca, Mg, Zn, Fe and other elements of group II. Titrate the soln. with a 0·1 *N* soln. of nickel diethyl phosphorodithioate in an acid medium (0·1 to 1 *N* HNO_3) with the use of a rotating platinum micro-anode at a potential of + 0·8 V *vs.* the S.C.E. Interfering elements are Hg, Ag, Cu, Cd, and other heavy elements that form sparingly soluble diethyl phosphorodithioates. *Visual titration*—On adding nickel diethyl phosphorodithioate to a soln. containing Pb, a white turbidity is formed. After a vigorous shaking this white turbidity changes to a fine flocculent ppt. and the supernatant liquid becomes completely clear. This change can be used as a readily detectable end-point. The soln. containing Pb (0·01 to 0·1 *M*) should be in a low, wide beaker placed on a black paper near the end-point, and should be shaken vigorously. W. ROUBO

2528. **Effect of aromatic amines on the discharge of lead ions at the dropping mercury cathode.** L. S. Relshakhrit and V. I. Vorob'eva. *Vestn. Leningr. Univ.*, 1958, No. 10, *Ser. Fiz. i Khim.*, (2), 101–108.—Electro-capillary curves from drop-time and potential measurements show that, in both *N* KOH and *N* KNO_3 soln., there is adsorption of aniline, toluidine and xylidine on the mercury drop. Desorption occurs at $\simeq -1{\cdot}0$ V and $\simeq -1{\cdot}2$ V, respectively, *vs.* the S.C.E. The limiting current for Pb^{2+} in these soln. is 20 to 30% less than that in soln. not containing aromatic amines. Their effect on $E_{\frac{1}{2}}$ for Pb is a shift of 0·16 to 0·19 V in the more negative direction with KOH soln. and a slight shift in the opposite direction with KNO_3 soln. G. S. SMITH

2529. **Detection of titanium with chromotropic acid.** L. Sommer (Inst. of Anal. Chem., Univ. Brno, Czechoslovakia). *Z. anal. Chem.*, 1958, **163** (6), 412–414.—*Procedure*—On to a spot-tile are placed one drop of weakly acid titanium soln., one granule of solid chromotropic acid and one granule of Na acetate. A stable red or orange coloration is formed at pH 2 to 5. The interference of anions and cations is discussed. B. B. BAUMINGER

2530. **Determination of titanium with cupferron. (Ethylenedinitrilo)tetra-acetic acid as masking agent.** K. L. Cheng (Metals Div., Kelsey-Hayes Co., New Hartford, N.Y.). *Anal. Chem.*, 1958, **30** (12), 1941–1945.—Under carefully controlled conditions only Ti, Ce and U give coloured complexes with cupferron that can be quant. extracted by 4-methylpentan-2-one. EDTA is used as a masking agent; too much inhibits the reaction of Ti with cupferron. The ratio of cupferron to Ti should be slightly $> 4:1$. A fresh aq. soln. of the reagent is added slowly to the test soln. (pH 5·5 to 5·7) containing EDTA and 0·5 μg to 0·5 mg of Ti. This soln. is extracted after 5 min. by shaking with the ketone for 1 min. and the Ti is determined spectrophotometrically. Beer's law is obeyed at 350, 400 and 425 mμ. Procedures are given for Ti in cast iron, steel, clay and nickel-base alloy.

P. D. PARR-RICHARD

2531. **Spectrophotometric determination of copper in titanium and titanium alloys by dithizone extraction.** H. W. Pender (Chase Brass and Copper Co., Inc., Waterbury, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1915–1917.—The procedure described is applicable to the range 0·0001 to 1% of Cu. The sample is dissolved in H_2SO_4, then oxidised with H_2O_2 and the Cu is complexed with dithizone. The coloured complex is extracted with CCl_4 and the extinction read at 520 mμ. The accuracy and precision are within 1 to 2%. Aluminium, Cr, Fe, Mn, Mo, Ni, Sn and Pb do not interfere. The effect of V, which tends to oxidise the dithizone soln. and so give low recoveries, can be overcome by the addition of hydroxylamine hydrochloride.

K. A. PROCTOR

2532. **Separation of titanium from accompanying elements by ion-exchange chromatography. III. Separation of titanium and zirconium.** T. A. Belyavskaya, I. P. Alimarin and I. F. Kolosova (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1958, **13** (6), 668–670.—The method described is suitable for the separation of Ti and Zr over the range of ratios from 1000:1 to 1:10,000. Pack a column (11 cm × 0·5 cm) with KY-2 resin in the hydrogen form, wash it with *N* HCl and introduce the test soln. (*N* with respect to HCl) containing the chlorides of titanium and zirconium. Wash the column with *N* HCl to elute titanium, then elute zirconium with 4 *N* HCl. W. ROUBO

2533. **Determination of reduced titanium chlorides in fused salt melts.** S. Mellgren and M. B. Alpert (Titanium Div., National Lead Co., Sayreville, N.J.). *Anal. Chem.*, 1958, **30** (12), 2061–2063.—Methods for the determination of total Ti, Ti^{II} and Ti^{III} in melts containing reduced titanium chlorides and alkali or alkaline-earth chlorides are described. Total Ti is determined by reduction to Ti^{III} and titration with $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln.; Ti^{II} is determined by reaction with H-saturated HCl to give H, the vol. of which is measured. The apparent valency of Ti is found by oxidation with H_2O_2 and titration with NaOH soln. to a bromothymol blue end-point. The methods are applicable only when the apparent valency is between 2 and 3.

P. D. PARR-RICHARD

2534. **Spectrophotometric determination of trace molybdenum and tungsten in titanium dioxide pigments using dithiol.** L. G. Stonhill (Laporte Titanium Ltd., Luton, England). *Chemist Analyst*, 1958, **47** (3), 68–69.—Fuse the pigment (1 g) with Na_2CO_3 (1·5 g) in a platinum crucible, grind the cold melt in a glass mortar, transfer it to a flask containing 15 ml of cold conc. HCl and leave overnight. Then add 15 ml of water, warm gently till dissolved, cool, and pass SO_2 for 2 min. Transfer to a separating-funnel, shake with 25 ml of dithiol soln. (0·1% in *n*-amyl acetate) and allow to separate. Retain the aq. phase for the determination of W, filter the organic phase, rejecting the first portion of the filtrate, and measure the transmission in a 4-cm cell at 670 mμ, referring the result to a standard curve prepared with sodium molybdate. For the determination of W, take a suitable aliquot (usually one-quarter) of the aq. phase, add 1 ml of $SnCl_2$ soln. (20% in conc. HCl), conc. HCl equal to the aliquot volume, and 20 ml of dithiol soln. Warm to 50° and shake for three 5-min. periods, re-heating between each. Run the organic layer into a 50-ml flask, make up to vol. with amyl acetate, filter as above, and read the transmission in a 4-cm cell at 640 mμ. Refer the results to a standard curve prepared with sodium tungstate. Chromium can be determined by dissolving the pigment (2 g) in HF, fuming with H_2SO_4, oxidising the soln. with Ag_2SO_4 and sodium bismuthate, and determining Cr colorimetrically with diphenylcarbazide. For the determination of V, the pigment (5 g) is fused with Na_2CO_3, the melt is dissolved in the minimum vol. of dil. H_2SO_4, the V is oxidised with $KMnO_4$, excess is removed with $NaNO_2$, excess of nitrite is removed with urea, and the V determined by potentiometric titration with 0·001 *N* $FeSO_4$.

R. E. ESSERY

2535. **Recent developments in analytical chemistry of zirconium.** E. B. Read and F. A. Bauman. *U.S. Atomic Energy Comm.*, Rep. TID-7555, 1958, 116–126.—Gravimetric, volumetric, colorimetric, spectrophotometric, spectrographic, X-ray fluorescent and vacuum-fusion methods for the determination of Zr and Hf are reviewed. (13 references.)

S.C.I. ABSTR.

2536. **Determination of zirconium in plutonium - zirconium alloys.** K. S. Bergstresser (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-1463 (Del.), Sept. 5, 1952. Decl. with deletions Oct. 5, 1956. 22 pp.—Such alloys were brought into soln. with a bisulphate fusion and the Zr was separated by pptn. with *p*-bromomandelic acid. Determinations were completed by weighing the zirconium oxide obtained after ignition of the ppt. at 925°. The precision of this recommended procedure was estimated in terms of the standard deviation for quadruplicate determinations, made with weight aliquots from dissolved alloy samples. The range for the standard deviation was 0·5 to 1·7 parts per thousand for samples from which aliquots each containing 9 to 15 mg of Zr were selected. The complete recovery of Zr from soln. of pure zirconyl chloride and plutonium trichloride was shown by the 95% confidence limits of 99·9 ± 0·3% for the average of four determinations, observed with samples containing 5 to 12 mg of Zr in the presence of 10 to 20 mg of Pu. It was found that Mo, La, Pu^{III} and $K_2Cr_2O_7$ do not interfere with determinations of Zr made according to the recommended procedure, but Pu^{IV} does interfere slightly. It was also observed that small amounts of Pu^{III} do not interfere with the colorimetric determination of Zr by means of a zirconium - alizarinsulphonate lake.

NUCL. SCI. ABSTR.

2537. **Spectrophotometric determination of iron in zirconium metal and in zirconyl chloride.** L. Silverman and K. Trego (Atomics International, Canoga Park, Calif.). *Anal. Chim. Acta*, 1958, **19** (3), 299–303 (in English).—Dissolve 1 g of zirconium (containing > 20 p.p.m. of Fe) in a platinum dish with 3 ml of H_2O by dropwise addition of 2·5 ml of HF. Add 4 ml of HCl and 1·2 g of H_3BO_3 and evaporate almost to dryness. Dissolve the residue in 75 ml of HCl (1:1). Transfer the soln. to a 150-ml beaker, add 1 to 2 drops of 30% H_2O_2 and evaporate to half volume. Transfer the soln. to a 100-ml flask and make up to volume with HCl (1:1). Measure the extinction at 360 mμ, and make a blank determination on Fe-free $ZrOCl_2$. The permissible range of Fe may be extended by taking a larger sample weight, and, after evaporating the chloride soln. almost to dryness, treating the residue with 10 ml of HCl (3:1) and filtering off the undissolved $ZrOCl_2$. The soln. is evaporated almost to dryness and the determination is completed as described above. The separated $ZrOCl_2$ is Fe-free. Similar procedures may be applied to $ZrOCl_2$. T. R. ANDREW

2538. **Determination of copper as an impurity in zirconium and Zircaloy.** G. W. Goward and B. B. Wilson (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-154 (Rev. 1), Apr. 16, 1957. 6 pp.—Copper forms a coloured complex with neo-cuproin (2:9-dimethyl-1:10-phenanthroline) in a $CHCl_3$ - ethanol system with a max. absorbance at 457 mμ. The method covers the determination of impurity copper in zirconium and Zircaloy in the range of 25 to 3000 p.p.m. on a 1-g sample basis. NUCL. SCI. ABSTR.

2539. **Tentative method for the determination of boron as an impurity in zirconium and Zircaloy.** G. W. Goward, H. R. Wilson and M. A. McCracken (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA-(GLA)-323, Jan. 25, 1957. 7 pp.—Zirconium or Zircaloy is dissolved in H_2SO_4. Boron is separated from the sample by distillation as methyl borate into a NaOH - methanol mixture. Methanol is removed by evaporation and B is determined spectrophotometrically as the curcumin complex in a methanol - oxalic acid soln. The method covers the determination of B in zirconium and Zircaloy in the range 0·1 to 0·7 p.p.m. on a 1-g sample basis. NUCL. SCI. ABSTR.

2540. **Determination of silicon as an impurity in zirconium and Zircaloy.** G. W. Goward, B. B. Wilson and S. Kallman (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-156 (Rev. 1), Apr. 29, 1957. 5 pp.—Hydrofluoric acid is used both to dissolve the sample and to convert the Si into a reactive form. The Si is caused to react with molybdic acid to form molybdosilicic acid, which is then reduced to a heteropoly blue complex. Photometric measurement is made at 815 mμ. The method covers the determination of Si as an impurity in zirconium and Zircaloy in the range of 10 to 200 p.p.m. on a 1-g sample basis. NUCL. SCI. ABSTR.

2541. **Determination of lead as an impurity in zirconium and Zircaloy.** G. W. Goward and B. B. Wilson (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-155 (Rev. 1), Apr. 23, 1957. 6 pp.—The sample is dissolved to give a soln. having a measured vol. and acidity. Citrate and cyanide are added, the soln. is adjusted to a pH of 9·0 to 9·5 and Pb is extracted with dithizone in $CHCl_3$. Separation from interfering elements is accomplished by extraction of the Pb back to a buffered aq. phase and subsequent re-extraction with $CHCl_3$ - dithizone from NH_4CN medium. The method covers the determination of impurity lead in zirconium metal and Zircaloy in the range of 50 to 500 p.p.m. on a 1-g sample basis. NUCL. SCI. ABSTR.

2542. **Determination of titanium as an impurity in zirconium and Zircaloy.** R. O. Backer and G. W. Goward (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-157 (Rev. 1), Apr. 18, 1957. 6 pp.—Titanium forms a yellow complex with H_2O_2 in a 1·5 to 3·5 *N* H_2SO_4 soln. The colour develops instantaneously and is stable for at least 24 hr. The max. absorbance of the complex is at 410 mμ. The method covers the determination of Ti as an impurity in zirconium and Zircaloy. The range of the method is from 10 to 100 p.p.m. on a 1-g sample basis. The principal sources of interference are V and Mo. These must either be removed or a correction made for them. The interference of coloured ions such as Fe, Ni and Cr^{3+} is compensated for by the use of a portion of the sample soln., not treated with H_2O_2, in the reference cell. NUCL. SCI. ABSTR.

2543. **Determination of molybdenum as an impurity in zirconium and Zircaloy.** G. W. Goward and R. M. Burd (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-192 (Rev. 1), Mar. 17, 1957. 4 pp.—Quinquevalent Mo reacts with thiocyanate in acid soln. to form a stable complex which is extracted with butyl acetate. The butyl acetate soln. of the complex exhibits an absorbance max. at 472 mμ. The method covers the determination of impurity Mo in zirconium and Zircaloy over the range of 5 to 50 p.p.m. on a 1-g sample basis. Tungsten interferes to the extent that 500 μg is equiv. to 0·9 μg of Mo. NUCL. SCI. ABSTR.

2544. **Determination of tungsten as an impurity in zirconium and Zircaloy.** K. L. Cheng, G. W. Goward and B. B. Wilson (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-180 (Rev. 1), Apr. 19, 1957. 5 pp.—The addition of $SnCl_2$ and KSCN to an acid tungstate soln. results in a coloured tungsten thiocyanate complex which exhibits max. absorbance at 400 mμ. The method covers the determination of W in the range from 25 to 400 p.p.m. on a 0·5-g sample basis. The effects of impurities and alloying additives in zirconium and Zircaloy are compensated for by the use of a blank consisting of a sample in which the thiocyanate colour has not been developed. Without a blank of this type the Cr and Ni interfere to the extent that they are coloured in soln. More than 0·1 mg of Cu present in the sample taken for analysis results in a ppt. of cuprous thiocyanate. Filtration before colour measurement eliminates this interference. NUCL. SCI. ABSTR.

2545. **Determination of chloride as an impurity in arc-melted zirconium and Zircaloy.** G. W. Goward, A. W. Perrine, J. F. Rodgers and H. R.

Wilson (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-193(Rev. 1), Apr. 18, 1957. 4 pp.—Chloride is pptd. as a suspension of AgCl by the addition of $AgNO_3$ to an acid soln. of the sample. The concn. of Cl^- is determined by nephelometric measurement of this suspension. The method covers the determination of 5 to 100 p.p.m. of Cl^- on a 1-g sample of zirconium or Zircaloy.

NUCL. SCI. ABSTR.

2546. **Determination of manganese as an impurity in zirconium and Zircaloy.** E. W. Beiter, R. M. Burd and G. W. Goward (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-182 (Rev. 1), Mar. 17, 1957. 4 pp.—In H_2SO_4 soln., Mn^{3+} are quantitatively oxidised to MnO_4^- by alkali periodates. The permanganate colour, which is stable in the presence of excess of periodate, exhibits an absorbance max. at 525 mμ. The interference of residual or alloying Fe, Cr and Ni is eliminated by discharging the permanganate colour in a portion of the sample soln. with sodium azide and using this soln. as a blank. The method covers the determination of Mn as an impurity in zirconium and Zircaloy in the range of 10 to 200 p.p.m. on the basis of a 1-g sample.

NUCL. SCI. ABSTR.

2547. **Tentative method for the determination of cobalt as an impurity in zirconium and Zircaloy.** P. Tate, H. R. Wilson, G. W. Goward and E. W. Beiter (Westinghouse Electric Corp., Bettis Plant, Pittsburgh, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WAPD-CTA(GLA)-326, Jan. 28, 1957. 5 pp.—Cobalt in buffered HF soln. is extracted with $CHCl_3$ as the nitrosonaphthol complex. The extract is evaporated to dryness, the organic material is destroyed, and the Co is caused to react with nitroso-R salt in hot acetate-buffered soln. to give a sol. red complex salt. Hydrochloric acid is then added to decompose nitroso-R complexes of other heavy metals. Cobalt is then determined by spectrophotometric measurement at 510 mμ. The method is applicable to the determination of Co in zirconium and Zircaloy in the concn. range of 0·5 to 30 p.p.m. on a 1-g sample basis.

NUCL. SCI. ABSTR.

2548. **Recent developments in analytical chemistry of thorium and its compounds.** C. V. Banks. *U.S. Atomic Energy Comm.*, Rep. TID-7555, 1958, 79–114.—Gravimetric, titrimetric, spectrophotometric and polarographic methods are reviewed and organic reagents employed are listed with appropriate data. (152 references.)

S.C.I. ABSTR.

2549. **The use of the indophenol blue reaction for the photometric determination of nitrogen.** U. Bohnstedt (Forschungsinst. der Dtsch. Edelstahlwerke, A.-G., Krefeld, Germany). *Z. anal. Chem.*, 1958, **163** (6), 415–422.—The spectrophotometric method described by Riley (*cf. Anal. Chim. Acta*, 1953, **9**, 575) has been adopted. Thus, $(NH_4)_2SO_4$ soln. (containing 0·02 to 0·18 mg of N) is placed in a 50-ml flask, mixed with 10 ml of Na phenoxide and set aside for 5 min. After addition of 5 ml of NaOCl soln. and 2 ml of $MnSO_4$ soln. the mixture is heated at 70° for 45 min. The soln. is cooled, diluted to 50 ml and the extinction measured at 600 mμ after 30 min. Blank determinations are carried out daily. The relative error is 2 to 3%.

B. B. BAUMINGER

2550. **Stable nitrogen isotope analysis by optical spectroscopy.** H. P. Broida and M. W. Chapman (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2049–2055.—The effect is described of operating conditions on the accuracy and precision of a method for determining the nitrogen isotopic concn. of nitrogen gas and NO gas by optical spectroscopy with photoelectric detection. A determination can be made on a sample of 20 ml, at a pressure of 1·5 mm of Hg, in approx. 10 min., with an accuracy of a few per cent.

K. A. PROCTOR

2551. **Physico-chemical method for the determination of gas composition and the rate of oxidation of nitric oxide during flow. I.** S. Hempel. *Roczn. Chem.*, 1958, **32** (6), 1321–1332.—The method and apparatus for determination, during flow, of the composition of a gas mixture consisting of NO and NO_2, after the oxidation of NO, are described. The gas composition is found by measuring the contraction of vol. at various intervals of time. The changes due to dissociation depend on the temp. Tables of results obtained at different temp. and degrees of dissociation are given.

H. DMOWSKA

2552. **Inorganic nitrate, nitrite or nitrate - nitrite. Rapid colorimetric determination of microgram quantities in aqueous solution.** F. L. Fisher, E. R. Ibert and H. F. Beckman (Agric. and Mech. Coll. of Texas, College Station, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1972–1974.—Inorganic NO_2^- and NO_3^- can be determined separately or together by varying the H_2SO_4 concn. after addition of brucine. *Procedure for total N*—Dilute the sample (containing $\geq$15 μg of N) to 15 ml with H_2O in a 50-ml flask. Add 1 ml of 2% aq. brucine hydrochloride soln. and then 5 ml of conc. H_2SO_4. Set aside for 3 min. to develop colour due to NO_2^-, then add 10 ml of conc. H_2SO_4 to develop colour due to NO_3^-. Cool to 30° in the dark and read at 410 mμ. *For NO_3^- (NO_2^- present)*—Dilute the sample to 25 ml with H_2O, add 1 ml of reagent and then 5 ml of conc. H_2SO_4. Cool to 30° and read as before. *For NO_3^- (NO_2^- absent)*—Dilute the sample to 15 ml, add 1 ml of reagent, then 15 ml of conc. H_2SO_4. Cool to 30° and read as before. Agreement with the phenoldisulphonic acid method is excellent; the precision for 15 μg of N is ± 2%.

P. D. PARR-RICHARD

2553. **Direct titration of potassium ferricyanide with hydrazine sulphate in presence of zinc sulphate. Determination of hydrazine.** Bharat R. Sant (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 205–208 (in English).—Potassium ferricyanide may be titrated with 0·01 *M* hydrazine sulphate containing 35·44 g of $ZnSO_4$ per litre. The end-point is detected by the decolorisation of the ferricyanide soln. Good results are claimed for from 2 to 34 mg of hydrazine sulphate in a medium which may range from pH 2 to an alkalinity equiv. to 0·8 *N* NaOH.

T. R. ANDREW

2554. **Rapid determination of phosphorus in condensed sodium phosphates.** S. Zechner and V. Reppestam (Lab. Reymersholms Gamla Ind. Aktiebolag, Hälsingborg, Sweden). *Z. anal. Chem.*, 1958, **163** (6), 423–427.—*Procedure*—To 4 g of sample (for <40% of P_2O_5, 8 g) is added 20 ml of conc. HCl; the mixture is boiled carefully for 2 min., then transferred to a 1-litre flask and diluted to the mark

with water. A 25-ml aliquot is placed in a 300-ml conical flask, 15 ml of conc. HCl and 150 ml of Chimolac soln. (quinoline - molybdate - acetone) are added and the soln. is heated to 75°, without stirring, then filtered, and the ppt. is washed 5 or 6 times with 0·2 *M* KNO_3. The filter-paper pulp and ppt. are transferred to another flask, 50 ml of H_2O and an excess of standard NaOH soln. are added and the soln. is back-titrated with standard HCl soln., with phenolphthalein as indicator. The determination can be carried out in 15 to 18 min. For 10 analyses of technical sodium triphosphate, a coeff. of variation of 0·13% of P_2O_5 was obtained. A direct potentiometric titration is also described.

B. B. BAUMINGER

2555. **Turbidimetric determination of glassy phosphates employing o-tolidine.** L. E. Cohen (Food Machinery and Chem. Corp., Westvaco Min. Prod. Div., Carteret, N.J., U.S.A.). *Chemist Analyst*, 1958, **47** (3), 65–67.—The reaction of long-chain polyphosphates with *o*-tolidine (**I**) in acetic acid involves 1 mol. of **I** with 2 atoms of P. The reagent (stable for 10 days) is prepared by dissolving 0·5 g of **I** in 4·8 ml of glacial acetic acid and making up to 100 ml with 10% aq. mannitol soln. The sample (10 to 120 mg) is freed from organic matter by extraction with suitable solvents, dissolved in 40 ml of water and 10 ml of glacial acetic acid, and made up to 100 ml with water after filtration and washing if required. An aliquot (10 ml) is mixed with 5 ml of glacial acetic acid and 5 ml of reagent, air-bubbles are allowed to disperse, and the turbidity is read within 15 min. in a 10-mm cell at 425 mμ. Results are referred to a calibration curve, which is best prepared with a glass of the composition of that present in the sample or with one containing between 63·0 and 69·6% of P_2O_5. Ortho-, pyro-, tri- and trimeta-phosphates do not interfere, nor do sulphate, metasilicate, chloride, borate, nitrate and non-ionic surface-active substances; anionic surface-active substances and oxidising agents (perborates, peroxides, hypochlorites) must be removed. The final pH should be < 7, to avoid pptn. of **I**; chromatographic or ion-exchange procedures should be used to separate mixtures of components.

R. E. ESSERY

2556. **Colorimetric determination of bismuth in alloys.** M. P. Grotheer and J. L. Lambert (Dept. of Chem., Kansas State Coll., Manhattan). *Anal. Chem.*, 1958, **30** (12), 1997–1999.—At pH 2·3 to 3·0, Bi gives a ppt. with Amaranth dye. The ppt. is dissolved in 1% $Na_2HPO_4.7H_2O$ soln. and the extinction of the free dye so obtained is measured at 521 mμ. By amalgamating the alloy with mercury and dissolving in cold H_3BO_3 - HNO_3, interference by Sn is avoided; other elements commonly present in bismuth alloys do not interfere. The max. error is $< 4\%$.

P. D. PARR-RICHARD

2557. **Determination of uranium, zirconium, magnesium and iron in bismuth alloys.** K. W. Kirby and R. H. A. Crawley (British Thomson-Houston Co. Ltd., Rugby, England). *Anal. Chim. Acta*, 1958, **19** (4), 363–368.—The recommended procedures are as follows. *Uranium*—Dissolve 0·2 g of the alloy in 2 ml of conc. HNO_3, evaporate until salts separate, add 1 ml of conc. HCl, dilute, and add 2·5 g of EDTA and excess of dil. aq. NH_3. Adjust to pH 7·0 with dil. acetic acid, add 2 ml of a 5% soln. of 8-hydroxyquinoline in ethanol and extract with 5 ml of $CHCl_3$. Add a further 2 ml of 8-hydroxyquinoline soln. and extract with two 5-ml portions of $CHCl_3$. Dilute the extracts to 20 ml with $CHCl_3$ and determine the extinction at 400 mμ in a 4-cm cell. Prepare a calibration curve, applying the same procedure to soln. of pure bismuth with known additions of U and 100 μg of Zr. The range is 20 to 1000 p.p.m. of U. Iron, Mg, Mn and Ni do not interfere. *Zirconium*—Dissolve a 0·5-g sample in 5 ml of dil. HNO_3 (1 + 1), add 0·75 ml of conc. $HClO_4$, evaporate to fuming and remove the excess of $HClO_4$ by heating at 200° for 15 min. Dissolve the residue in 14 ml of water, add 2·5 ml of conc. HCl and 5 ml of filtered 0·1% aq. soln. of alizarin red S. Heat in boiling water for 3 min., cool, dilute to 25 ml, set aside for 15 to 30 min. and measure the extinction at 560 mμ in a 4-cm cell. Iron (up to 500 μg), U, Mg, Ni and Mn do not interfere. *Magnesium*—Dissolve a 0·4-g sample in 5 ml of conc. HNO_3, add 2 ml of conc. $HClO_4$ and evaporate to vigorous fuming. Dissolve the residue in 10 ml of 20% HCl, add 10 ml of 20% NH_4I soln. and transfer to a separating-funnel with 10 ml of water. Extract the bulk of the BiI_3 with two 40-ml portions of *iso*butyl methyl ketone. To the aq. layer add 2 ml of a 2% soln. of 8-hydroxyquinoline in 2 *N* acetic acid and bring to pH 6 to 7 with aq. NH_3 soln. Extract the 8-hydroxyquinoline complexes of U, Zr, Fe, Ni and residual Bi with two 20-ml portions of $CHCl_3$. Evaporate the aq. layer to 20 ml, cool, add 1 ml of the 8-hydroxyquinoline soln. and 30 drops of aq. NH_3 soln. to produce a pH >10. Digest for 30 min. on a water bath, allow to cool for 30 min., and centrifuge. Wash the ppt. with three 3-ml portions of 4% aq. NH_3 soln., dissolve it in 6 drops of conc. HCl and dilute to 20 ml with water. Measure the extinction at 365 mμ in a 1-cm cell. Prepare a calibration graph by the same method with quantities of Mg up to 250 μg. *Iron*—Dissolve a 0·5-g sample in 1 ml of conc. HNO_3 and 2 ml of water, add 1·5 ml of conc. $HClO_4$ and evaporate to vigorous fuming. Dissolve the residue in 16 ml of water, add 3 ml of conc. HCl and 10 ml of a soln. prepared by dissolving 20 g of NH_4SCN in water, diluting to 80 ml, adding 2·5 ml of *N* HCl and extracting with two 10-ml portions of *iso*butyl methyl ketone. Extract the $Fe(SCN)_3$ with two 5-ml portions of *iso*butyl methyl ketone, dilute the extracts with the ketone to 20 ml and measure the extinction in a 2-cm cell, with an Ilford No. 603 filter. The calibration graph is prepared with the use of a soln. of pure bismuth with known additions of Fe. None of the metals likely to be present interferes.

H. N. S.

2558. **Determination of vanadium in petroleum residues.** Z. Řezáč and J. Dvořák (Res. Inst. Inorg. Chem., Ústí nad Labem, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (8), 409–411.—After dissolving the sample, V is oxidised to vanadate and determined amperometrically (vibrating platinum electrode) with quinol soln., which is a stable reductimetric reagent (*cf.* Simon and Zýka, *Anal. Abstr.*, 1956, **3**, 2945). *Procedure*—Ignite the sample (20 g) in a platinum dish at 500° to 600° till organic compounds and carbon are destroyed. Cool, add H_2SO_4 (1 + 1) (10 ml) and HF (10 ml) and evaporate on a sand bath. Repeat this procedure until dissolution is complete. Evaporate to dryness, heat the residue till white fumes appear, cool and dilute with H_2O (10 ml). Transfer with H_2O (10 ml) to a 100-ml flask (when large amounts of V are present, dilute to vol. and use an aliquot), add Na_2SO_3 (0·1 g), and 0·1 *N* $KMnO_4$ dropwise to a pink coloration. Set aside for 2 min., add a few

mg of $NaNO_3$ and then sulphamic acid (0·2 g). After 2 min., titrate at 1·0 V with 0·1 *N* to 0·005 *N* quinol. With a medium of 0·7 *N* to 9 *N* H_2SO_4, the results were in good agreement with theoretical values when determining 0·05 to 15 mg of V. Copper, W and an excess of Mo, Cr and Fe do not interfere. The interference of dichromates can be avoided by a selective reduction. J. ZÝKA

2559. **New methods for microchemical detection of vanadium and titanium [in mineral raw materials and steel].** K. P. Stolyarov. *Vestn. Leningr. Univ.*, 1958, No. 10, *Ser. Fiz. i Khim.*, (2), 122–125.—For Ti, the absorption band at 365 mμ of metatitanic acid pptd. by 2 *N* aq. NH_3 saturated with NH_4Cl is used for detection. The method is applied to steel and sulphide ores. No separations are necessary. The minimum amount detectable is 0·5 μg of Ti. With 1·0 μg of Ti, 50,000 times as much Al, Cr, V, Cu, Pb and Cd and 10,000 times as much Fe, Mn, Bi and Ag cause no interference. For V, the red colour assumed by lead vanadate when examined in a u.v. microscope is used. The sample of steel or ore is decomposed by normal methods, Fe, Mo and certain other elements are extracted with ether, the aq. soln. is evaporated to dryness, the residue is treated with HNO_3 which is evaporated off, and the residue is then dissolved in water and treated with Na_2SO_3 and 10% NaOH soln. to precipitate hydroxides. The soln. after filtration is boiled with HNO_3, then neutralised with NaOH, followed by acidification with acetic acid, and boiled to low bulk. A drop on a quartz slide is mixed with a drop of saturated Pb acetate soln. and the ppt. is examined under u.v. light. The minimum amount of V detectable is 0·03 μg. G. S. SMITH

2560. **Separation of niobium from zirconium by means of selenous acid.** I. P. Alimarin and E. I. Stepanyuk (M. V. Lomonosov Inst. of Fine Chem. Technol.). *Zavod. Lab.*, 1958, **24** (9), 1064–1065.—The method is based on the quant. pptn. of Nb by selenous acid in the presence of tartaric acid, which serves to retain Zr in soln. The method is unsatisfactory for the separation of Ta from Zr since some of the Ta is retained in soln. but, with Nb present as well, Ta is co-pptd. with the Nb and the degree of separation improves with increase in the content of Nb. G. S. SMITH

2561. **Determination of small amounts of tantalum in NaF - LiF - KF and in NaF - LiF - KF - UF_4.** J. C. White (Oak Ridge National Lab., Tenn.). *U.S. Atomic Energy Comm.*, Rep. CF-56-1-49, Jan. 10, 1956. Decl. Sept. 26, 1958. 10 pp.—The pyrogallol method was modified for this determination. In order to prevent the loss of tantalum as the volatile fluoride during dissolution of the samples, tantalum fluoride was hydrolysed with dil. H_2SO_4 before the complete removal of F^-, which interfere with this method, by heating in conc. H_2SO_4. Since uranium also interferes with the pyrogallol method, quadrivalent uranium was oxidised to uranyl, and tantalum was separated from the oxidised uranium by pptn. with cupferron in a conc. H_2SO_4 soln. The coeff. of variation for the determination of tantalum in both types of sample was 2%. NUCL. SCI. ABSTR.

2562. **X-ray spectrophotographic determination of tantalum, niobium, iron and titanium oxide mixtures using simple arithmetic corrections for inter-element effects.** B. J. Mitchell (Electro Metallurgical Co., Niagara Falls, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1894–1900.—*Cf. Proc., Conf. Ind. Appl. X-Ray Anal., 6th, Denver; Anal. Abstr.*, 1959, **6**, 528. K. A. PROCTOR

2563. **Analysis of sodium sulphide.** Society of Leather Trades' Chemists, Committee for Sulphide Analysis. *J. Soc. Leath. Tr. Chem.*, 1958, **42** (9), 294–297.—The iodine method described is not suitable for use with lime liquors. The ground sample is dissolved in "glycerine water" (boiled-out water containing 5% of glycerol), and this soln. is used for the determination of NaHS, NaOH, $Na_2S_2O_3$ and Na_2SO_3. Total sulphide is determined by treatment of the soln. with $ZnCO_3$ suspension, dissolution of the resulting ZnS with dil. HCl in the presence of iodine, and titration of the excess of iodine with $Na_2S_2O_3$ soln. Alternatively, the sample soln. is treated directly with iodine and acetic acid, and titrated with $Na_2S_2O_3$ soln. For the determination of NaHS or free NaOH, a known vol. of NaOH soln. is added to the sample soln., followed by $BaCl_2$ soln. The ppt. is filtered off, acidified cadmium ammonium chloride soln. is added, the ppt. is filtered off and the acidity in the filtrate is titrated with NaOH soln. The percentages of NaHS and NaOH are derived from given equations. For the determination of $Na_2S_2O_3$ and Na_2SO_3, sulphide is pptd. from the sample soln. by addition of $ZnCO_3$ suspension. One aliquot of the filtrate is titrated with iodine soln. in the presence of acetic acid, formaldehyde and starch soln., to give the $Na_2S_2O_3$ content, and another aliquot is treated with acetic acid and excess of iodine soln., then titrated with $Na_2S_2O_3$ soln. The Na_2SO_3 content is calculated from the difference between the two titrations. C. A. SLATER

2564. **Liquid scintillation counting of radioactive sulphuric acid and other substances.** N. S. Radin and R. Fried (Northwestern Univ. Med. School, Chicago, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1926–1928.—Sulphur-35 in large amounts of H_2SO_4 can be determined by liquid scintillation counting after converting the acid into the neutral salt of a high-mol.-wt. aliphatic primary amine and dissolving the salt in toluene - ethanol. The efficiency of counting is almost independent of the amount of sulphate, but does depend on the amount of amine. The method can be applied to other acids such as radioactive citric, phosphoric and hydrochloric acids. K. A. PROCTOR

2565. **Determination of sulphates by reduction to hydrogen sulphide.** I. I. Volkov and E. A. Ostroumov (Inst. Oceanology, Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (6), 686–690.—Carbon dioxide which has passed through copper sulphate, water, conc. H_2SO_4 and $CaCl_2$ is introduced into a reaction vessel which should contain an amount of sample such that sulphate calculated as sulphur is within the range 0·5 to 5 mg; 8 ml of reducing agent ($SnCl_2$ - anhyd. H_3PO_4, preparation described) is added, and CO_2 is passed through the system to remove all air. The reaction vessel is heated up slowly so that a temp. of 300° is reached in 15 to 20 min. Reduction begins at about 120°, and should be complete in 25 to 30 min. after 300° has been reached. The H_2S liberated is absorbed in Cd acetate soln. in two flasks. The first contains 25 ml of soln. (25 g of Cd acetate dihydrate and 1 ml of acetic acid per litre) diluted with water to 80 to 90 ml. The second flask contains 15 ml of the same soln. diluted with water up to 50 to 70 ml and acidified with 2 ml of acetic

acid. When the reduction is complete, the absorbing vessels are removed and the cadmium sulphide is dissolved in an acidified 0·02 *N* soln. of iodine. The flasks are stoppered, set aside for 20 to 30 min., and the excess of iodine is titrated with $Na_2S_2O_3$ soln. The method was tested with pure salts. It has been confirmed that Ca, Ba, Fe, Al, Cr, Mn, Co, Ni and Zn do not interfere. In the presence of up to 0·2 g of alkali-metal chlorides, the speed of reduction increases. Bismuth, Pb and Cd do not interfere in the reduction; Cu and Hg interfere. The method has been tested on natural materials such as gypsum, sea silt and sea water. W. ROUBO

2566. **Infra-red spectrum of sulphuryl bromofluoride.** T. T. Crow and R. T. Lagemann (Vanderbilt Univ., Nashville, Tenn., U.S.A.). *Spectrochim. Acta*, 1958, **12** (2–3), 143–146.—The i.r. absorption spectrum of gaseous SO_2BrF has been observed by using a prism spectrometer equipped with sodium chloride, potassium bromide and caesium bromide prisms. Of the nine fundamental vibrations, eight have been observed. In the absence of the necessary Raman data some of these fundamentals have been left unassigned.
E. G. CUMMINS

2567. **Separation of tellurite, selenite and sulphite ions by anion-exchange resins.** Akira Iguchi (Chem. Dept., Coll. of Gen. Educ., Univ. of Tokyo, Meguro-ku). *Bull. Chem. Soc. Japan*, 1958, **31** (6), 748–752.—The distribution coefficients of tellurite, selenite and sulphite in neutral nitrate soln. and in alkaline hydroxide soln. are measured. The results suggest the presence of an acid-salt ion HXO_3^- in neutral soln. By adding aq. NH_3 to the eluent soln., the distribution coefficient of the salts in nitrate soln. is increased, but is in hydroxide soln. decreased. The addition of ethanol to the eluent soln. containing nitrate and aq. NH_3 increases the distribution coefficient of sulphite, but that of tellurite and selenite remains constant even up to 75% of ethanol. With hydroxide soln., the coefficient of sulphite decreases, while that of tellurite and selenite increases at first and then decreases. A complete separation of tellurite, selenite and sulphite is accomplished by anion-exchange chromatography with an alkaline eluent. I. JONES

2568. **Rapid method of determining selenium in materials for sulphuric acid manufacture.** F. N. Kel'man (Ya. V. Samollov Sci. Inst. of Fertilisers and Insectofungicides). *Zavod. Lab.*, 1958, **24** (9), 1061–1064.—The sample is decomposed in a tube at 750° in a current of air enriched with oxides of N, the SeO_2 is collected from the gas, and the content of Se is finally determined by titration of the iodine liberated from KI in the presence of HNO_3, after destruction of HNO_2 with urea. G. S. SMITH

2569. **Determination of chromium by a solvent-extraction method.** P. D. Blundy (Chem. Engng Div., A.E.R.E., Harwell, Berks., England). *Analyst*, 1958, **83**, 555–558.—An aliquot of the sample soln. (≡ 10 to 90 μg of Cr) is neutralised with aq. NH_3 and slightly acidified with dil. H_2SO_4. Any Fe^{3+} present are oxidised by addition of 0·02 *N* ammonium hexanitratocerate. The soln. is then treated with 4 *N* H_2SO_4 and 0·02 *N* ammonium hexanitratocerate, diluted and heated in boiling water. It is then cooled to < 10° and 4 *M* HCl is added while the liquid is cooling. The chromate is extracted from the cold acid liquid with *iso*butyl methyl ketone previously saturated with 4 *M* HCl, and the aq. layer is discarded. The ketone layer is extracted twice with water, the acidified aq. extract is treated with diphenylcarbazide soln. (1% in acetone), adjusted to a known vol. and its extinction is measured in a Spekker absorptiometer with a mercury-vapour lamp and Ilford No. 605 filters. The calibration graph is prepared with standard soln. of chromium potassium sulphate to which interfering elements in the concn. expected in the sample soln. have been added. In the presence of 100 μg each of Ni and Fe, Cr was determined in the range 10 to 100 μg with a mean recovery of 100·3% and a standard deviation of ± 0·8%.
A. O. JONES

2570. **Solvent extraction of chromium with acetylacetone.** J. P. McKaveney and H. Freiser (Dept. Chem., Univ., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1965–1968.—Unlike Al, Fe, V, Mo and Ti, Cr does not readily form a complex with acetylacetone (**I**). The former cations may therefore be removed by extraction with **I** at pH 2; Cr in the aq. layer is determined by adjusting the soln. to pH 7 and heating it under reflux with **I**. *Procedure for ferrous alloys*—Dissolve 1 g of alloy in dil. HCl - H_2SO_4, oxidise with HNO_3 and filter. Evaporate to 25 ml, add conc. aq. NH_3 to pH 2·0 and shake with **I**. Readjust the aq. layer to pH 2·0 and shake with $CHCl_3$, then with $CHCl_3$ - **I** (1:1). Neutralise the aq. layer with conc. aq. NH_3 and add 2 ml in excess, then 30 ml of **I**. After heating the mixture for 30 min. under reflux, remove the organic phase containing Cr, and wash the aq. layer with $CHCl_3$. Back-wash the combined organic layers with 6 *N* H_2SO_4, washing this in turn with $CHCl_3$. Combine the organic extracts, make up to 50 ml with **I** in the presence of 2 g of anhyd. Na_2SO_4 and measure the extinction at 560 mμ. For samples containing < 0·2% of Cr, isolate the Cr with **I** and determine by the diphenylcarbazide procedure.
P. D. PARR-RICHARD

2571. **Decomposition of cyanate in acid solution with reference to the analysis of chromium-bearing minerals and alloys.** E. Bishop (Washington Singer Lab., Univ., Exeter, England). *Analyst*, 1958, **83**, 588–591.—To avoid the formation of chromammines in the determination of Cr in rocks and steel, the NH_3 serving as precipitant is introduced slowly by hydrolysis of a cyanate. When this method is applied to chromite, an insol. decomposition product of the cyanate is pptd. with the Cr, and this interferes with the gravimetric and to some extent with the titrimetric determinations. Investigation of the decomposition products of NaCNO showed that this interfering substance is sodium dihydrogen cyanurate and the mechanism of its formation is discussed. The interference does not occur in the presence of HNO_2 or HNO_3 owing, it is considered, to removal by the HNO_3 or reduced HNO_2 of the catalyst effecting polymerisation of HCNO, *viz*, urea. In using cyanate for the pptn. of hydrated oxides in chromite analysis one of the following procedures is recommended—(*a*) leaching of the peroxide-fusion product with HNO_3, reduction of the chromate with SO_2 and dehydration of the silica with HNO_3; (*b*) use of HCl up to the second silica dehydration and extraction of the baked residue with HNO_3; (*c*) use of HCl throughout, with addition of a small amount of $NaNO_2$ before the addition of cyanate. A. O. JONES

2572. **Determination of tungsten or molybdenum by X-ray emission spectrography.** J. E. Fagel, jun., H. A. Liebhafsky and P. D. Zemany (Res. Lab., General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1918–1920.—In alkaline soln. W can be determined in about 30 min. with Br as an internal standard. The observed standard deviation, at a concn. of W of 0·01%, is about 50% larger than the unavoidable counting errors. In small amounts Mo can be determined by measuring the ratio of Mo K_α to W $L\gamma_1$. The precision is considerably lower for powders analysed directly than for samples in aq. soln. Background correction is discussed.

K. A. PROCTOR

2573. **Analysis of uranium and its compounds.** C. J. Rodden. *U.S. Atomic Energy Comm.*, Rep. TID 7555, 1958, 24–42.—The various methods employed are reviewed and the titration of U as a function of $K_2Cr_2O_7$ concn. is discussed, a similar degree of variation being noted with $Ce(SO_4)_2$: isotopic analysis is also reviewed. Impurities present in uranium compounds are examined in some detail and the freezing-point of UF_6 is discussed as it has proved a satisfactory method of determining the total soluble impurities. (32 references.) S.C.I. ABSTR.

2574. **Determination of uranium in ores, leach solutions and mill products.** M. A. DeSesa. *U.S. Atomic Energy Comm.*, Rep. TID 7555, 1958, 57–77.—Volumetric and polarographic (with simultaneous determination of U and V), fluorimetric (LiF - NaF flux) and spectrophotometric methods are briefly reviewed. The design of the fluorimeter and the results obtained with different equipment and different fluxes are presented. S.C.I. ABSTR.

2575. **Use of organic reagents in inorganic analysis. VIII. Spectrophotometric determination of uranium with 2-hydroxy-1-nitroso-3-naphthoic acid.** Sachindra Kumar Datta (Darjeeling Gov. Coll., India). *Z. anal. Chem.*, 1958, **163** (6), 403–408 (in English).—The method is based on the dissolution of the uranyl complex of 2-hydroxy-1-nitroso-3-naphthoic acid in 3 *M* aq. NH_3, and measurement of the extinction of this soln. in 1-cm cells at 430 mμ. The optimum pH range is between 8 and 11. The method is useful since foreign ions can be separated from the uranium soln. before its photometric determination; it is, however, not possible to determine < 2 mg per 25 ml by this method.

B. B. BAUMINGER

2576. **Tungsten interference in the volumetric analysis of uranium.** R. F. Dufour and O. J. Articolo (Knolls Atomic Power Lab., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KAPL-M-RFD-2, Aug. 4, 1958. 9 pp.—Tungsten was found to have a negligible effect on the determination of U in uranium - zirconium alloys by the Jones reductor - dichromate method used at Knolls Atomic Power Lab. The tungstate ion seriously interfered and caused high results. However, the soluble tungsten was pptd. by intense fuming with H_2SO_4 and rendered ineffective in the subsequent oxidation - reduction reactions of the uranium.

NUCL. SCI. ABSTR.

2577. **Determination of uranium in uranium hexafluoride material.** C. A. Kienberger (Union Carbide Nuclear Co., Oak Ridge, Tenn., U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 338–341.—A method is described for the determination of U in technical uranium hexafluoride that contains only volatile impurities such as HF and fluorocarbons. A sample (7 g) of the material is transferred in a vacuum system to a fluorothene tube; it is frozen with liq. nitrogen, and helium is admitted to the tube, which is then weighed. The UF_6 is hydrolysed by submerging the uncapped tube in ice-cold water (150 ml), the soln. is evaporated to dryness and the residue ignited at 850°. The resulting oxide is weighed and the weight is corrected for any metallic impurities found by spectrographic examination. H. N. S.

2578. **Plant-type polarographic system for determining uranium in radioactive waste streams.** G. J. Alkire, K. Koyama, K. J. Hahn and C. E. Michelson (General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1912–1915.—The equipment described is designed for in-line use and records the uranium concn. in the range 10^{-4} to 10^{-2} *M* every 7·5 min. A HNO_3 electrolyte is used and in this U^{VI} is reduced to U^{V} at the dropping mercury electrode. Nitrite, Fe and tributyl phosphate do not interfere significantly. The over-all precision in routine operation is ± 10%.

K. A. PROCTOR

2579. **Quantitative determination of uranium and beryllium in fused-salt systems.** N. E. Rogers and W. D. Prather (Mound Lab., Miamisburg, Ohio, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. MLM-1070, Apr. 3, 1956. Decl. July 11, 1957. 15 pp.—A method is described for the quant. separation and determination of U and Be in the presence of macro quantities of Na in a ternary system of fused fluorides. The F^- are volatilised as fluoroboric acid during the dissolution of the dried mixed salts with acids. The separation of U from Be and Na is accomplished by the electrolytic deposition of the U as a hydrous oxide on a platinum electrode from a hot ammonium acetate soln. at pH 4·0. The Be remains in the plating soln. with the Na, and is determined as the hydroxide. Both the deposit of U and the $Be(OH)_2$ ppt. are ignited and weighed as their respective oxides. Sodium is determined flame-photometrically, or it may be calculated as the difference between the combined weights of the uranium and beryllium fluorides and the original sample weight. NUCL. SCI. ABSTR.

2580. **Polarographic determination of uranium in uranium - zirconium alloys and in uranium oxide - alumina ceramics.** J. T. Porter, II (Knolls Atomic Power Lab., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KAPL-M-JTP-3, Aug. 5, 1958. 17 pp.—The precision of this analysis is ≃ 0·6% relative. The procedure is simple, involves no separations, and is free from interference by W, Cu and Fe in amounts normally present in fuel alloys and ceramic materials. NUCL. SCI. ABSTR.

2581. **Separation of uranium from diverse ions.** W. J. Maeck, G. L. Booman, M. C. Elliott and J. E. Rein (Atomic Energy Div., Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1902–1907.—*Cf. U.S. Atomic Energy Comm.*, Rep. IDO-14415, 1957; *Anal. Abstr.*, 1958, **5**, 3718.

P. D. PARR-RICHARD

2582. **Separation of small amounts of scandium from uranium.** K. S. Bergstresser (Los Alamos Scientific Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LAMS-1674, May, 1954. Decl. Oct. 1,

1958. 15 pp.—A method for separating small amounts of Sc (1 to 10 mg) from 1 g of uranium depends on the formation of insoluble uranium peroxide while the Sc in soln. is complexed with EDTA. The pptd. peroxide carries down < 30 p.p.m. of Sc. Uranium left in soln., < 1 mg, does not interfere when the Sc is pptd. as ammonium scandium tartrate and determined gravimetrically by ignition of the tartrate to the oxide.

NUCL. SCI. ABSTR.

2583. **Ion-exchange spectrographic method for determination of impurities in uranium and plutonium.** J. K. Brody, J. P. Faris and R. F. Buchanan (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1909–1912.—The sample metal is dissolved in 12 *N* HCl and a few drops of conc. HNO_3 and applied to a Dowex-1 ion-exchange column. The impurities are eluted with HCl of various concn. and determined spectrographically by the copper-spark method.

K. A. PROCTOR

2584. **Determination of boron in uranium-zirconium fuel.** V. F. Consalvo (Knolls Atomic Power Lab., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KAPL-M-VFC-4, Sept. 2, 1958. 8 pp.—A combination of the H_2SO_4 dissolution procedure and the carminic acid method has been applied with some modifications to the determination of B in uranium-zirconium fuel clad with Zircaloy-H. The procedure was developed on "as received" fuel in preparation for the determination of residual B in irradiated samples.

NUCL. SCI. ABSTR.

2585. **Effect of plutonium on the fluorimetric determination of uranium.** K. S. Bergstresser (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-1707, July, 1954. Decl. July 27, 1956. 23 pp.—The fluorimetric method for determining microgram quantities of U dissolved in conc. H_2SO_4 was re-investigated for the purpose of measuring any interference caused by Pu in uranium samples. No plutonium fluorescence, and therefore no positive errors due to Pu, was observed. Limited transmittance of Pu^{4+} in H_2SO_4 at 513 mμ, and especially at 360 mμ, produces variable negative errors in uranium determinations.

NUCL. SCI. ABSTR.

2586. **Spectrochemical analysis of plutonium and its compounds. II. The cupferron procedure.** N. H. Nachtrieb, H. A. Potratz, O. R. Simi, S. Wexler and B. S. Wildi (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-387 (Del.), Sept. 14, 1945. Decl. July 19, 1957. 33 pp.—A method is described whereby milligram samples of Fe, Sb, V, Ta, Ti, Nb, Zr, Sn, Bi, U or Pu may be analysed for p.p.m. of 39 impurity elements. The procedure consists in forming the acid-insoluble cupferride of one of the elements named and extracting the compound from the impurities by means of $CHCl_3$. The aq. soln. containing the impurities is evaporated on copper electrodes which are sparked to produce the spectrum of the impurity.

NUCL. SCI. ABSTR.

2587. **Rapid simultaneous determination of plutonium(IV) and americium(III) in nitric acid solution.** T. Bruce (Atomic Energy of Canada Ltd., Chalk River Project, Ont.). *U.S. Atomic Energy Comm.*, Rep. CRDC-805, Aug. 1958. 13 pp.—Zirconium is added to the soln. to be analysed as a carrier for the Pu, and phenylarsonic acid is added as a precipitant. The Zr together with the Pu is pptd., leaving the Am in the supernatant phase. The Am and Pu are then determined by α-counting. The Am values obtained are ≃ 5% high and the Pu values are low by a similar amount. The precision attained is about ± 2%.

NUCL. SCI. ABSTR.

2588. **The chemical analysis of ternary alloys of plutonium with molybdenum and uranium.** G. Phillips, J. Woodhead and E. N. Jenkins (Chem. Div., A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1958, **19** (3), 229–234 (in English).—Molybdenum is determined photometrically at 500 mμ as the reduced thiocyanate on an aliquot of the sample solution; U (up to 250 : 1) and Pu (up to 15 : 1) do not interfere. Molybdenum interferes in the determination of U and Pu by the Atkins and Jenkins method (unpublished), but can be separated from a second portion of the sample soln. by extraction of the benzoin α-oxime complex with $CHCl_3$ from 1·5 *N* $HClO_4$ soln.

T. R. ANDREW

2589. **Argentimetric titration of halide and cyanide ions with dithizone as indicator.** E. E. Archer (The Distillers Co. Ltd., Res. and Development Dept., Great Burgh, Epsom, England). *Analyst*, 1958, **83**, 571–579.—To titrate I^-, the sample soln. (≡ 0·05 to 0·2 milli-equiv. of I^-) is adjusted to 10 ml with water, 2 ml of dil. H_2SO_4, 50 ml of acetone and 1 ml of dithizone soln. (0·01% in acetone) are added, and the liquid is titrated with aq. 0·01 *N* $AgNO_3$, more dithizone soln. being added near the end-point at which the green of the dithizone changes to the orange-yellow of the silver dithizonate (keto form). With slight modifications, the titrations of Ag^+ with 0·01 *N* KI and of Br^- with $AgNO_3$ are similar. For Cl^-, 1 ml of the sample soln. (≡ 0·02 to 0·05 milli-equiv. of Cl^-) is treated with 50 ml of acetone, 0·02 ml of dil. H_2SO_4 and 1 ml of dithizone soln. (0·003% in acetone) and titration is with a 0·004 *N* soln. of $AgNO_3$ in *n*-propanol. In a modification involving preliminary evaporation of the slightly alkaline sample soln. (up to 50 μg of Cl^-), dissolution of the residue in 0·05 ml of water, and addition of 1 drop of dil. H_2SO_4 and 0·1 ml of 0·003% dithizone soln., the titration is made from an Agla syringe type micro-burette with magnetic stirring. Similar procedures are described for titration of CN^- with standard $AgNO_3$ soln. and the reverse titration, ethanol being the non-aq. solvent. With all these procedures, blank determinations are necessary. Applications to the determination of Cl in organic compounds after Carius digestion, determination of halogens in organic compounds and of CN^- in vinyl cyanide are described.

A. O. JONES

2590. **Fluorine analysis by pyrohydrolytic separation.** T. S. West (Univ. Birmingham, England). *Chem. Age*, 1958, **80**, 603.—A review is presented of recent work on the use of the method of "pyrohydrolysis" in the determination of F, particularly in rare earths. (10 references.)

2591. **The determination of fluorine in rare-earth fluorides by high-temperature hydrolysis.** C. V. Banks, K. E. Burke and J. W. O'Laughlin (Inst. for Atomic Research, Iowa State College, Ames, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 239–243 (in English).—The pyrohydrolysis technique of Warf *et al.* (*Anal. Abstr.*, 1955, **2**, 2413) has been extended to rare-earth fluorides. At 975° ± 25°, fluorides of Lu, Yb, Ce^{III}, Sc, Gd, Tb, Dy, Ho, Er and Tm

are hydrolysed in less than 30 min. Fluorides of Y, La, Pr, Nd, Sm and Eu need 45 to 250 min. By incorporating a tenfold excess of U_3O_8 or Cr_2O_3, this time may be reduced to between 25 and 60 min.
T. R. ANDREW

2592. **Infra-red spectral analysis for hydrogen fluoride.** D. F. Smith (Tech. Div., Union Carbide Nuclear Co., Oak Ridge, Tenn., U.S.A.). *Spectrochim. Acta*, 1958, **12** (2–3), 224–232.—Equations pertaining to the lines of the fundamental vibration rotation band of HF are given—

$$(i)\ A_0 = mp_{HF},$$

where A_0 is the absorbance at the peak of a line for pure HF at pressure p_{HF}, and m depends on the experimental conditions, and—

$$(ii)\ (A/A_0)^2 = 1 + (b/a)\ (p_b/p_{HF}),$$

where A is the same absorbance for an identical sample of HF at the same partial pressure p_{HF} when mixed with a foreign gas at a partial pressure p_b, and b/a is the ratio of the foreign gas broadening efficiency to the self-broadening efficiency, a ratio which may be considered independent of experimental conditions. Since m and b/a may be measured (b/a values for 20 different foreign gases are tabulated) for pure materials, these equations can be used in analyses for HF, and the need for calibration samples for each set of conditions is obviated.
E. G. CUMMINS

2593. **Methods of de Saint Venant and Mohr and use of statistical criteria.** A. G. Loscalzo and A. A. Benedetti-Pichler (City Coll., New York, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2018–2019.—Saint Venant's method for determining Cl^- [titration with $AgNO_3$ soln. in the presence of lime water (*Compt. Rend.*, 1846, **23**, 522)] is shown to be no worse than Mohr's, the latter being less precise when a large amount of $NaHCO_3$ is added for rapid treatment of an acid soln. Joint confidence ellipses relating to fitted regression equations have been drawn to illustrate these conclusions.
B. J. WALBY

2594. **The induced reduction of chlorate ions.** L. J. Csanyi and M. Szabó (Inst. for Inorg. and Anal. Chem., Univ. of Szeged, Hungary). *Talanta*, 1958, **1** (4), 359–366.—The reaction between $HClO_3$ and As_2O_3 is too slow for direct titration but is accelerated markedly by OsO_4. According to Gleu (*cf. Z. anal. Chem.*, 1933, **95**, 385), the determination can only be carried out by adding an excess of arsenite and back-titrating with $Ce(SO_4)_2$ or $KMnO_4$ soln. This induced reaction can be carried out only by oxidising agents which react in 1-equiv. steps, these including $Co_2(SO_4)_3$, $Mn_2(SO_4)_3$, $Ce(SO_4)_2$ and $KMnO_4$. $K_2Cr_2O_7$ being only a poor inducer of the reduction. Silver ions accelerate the reaction, which is stated to be due to the formation of As^{IV}, which reduces ClO_3^- very rapidly. The following procedure is advocated. Acidify the sample (containing 3 to 35 mg of ClO_3^-) with 10 to 25 ml of 20% H_2SO_4. Add 5 to 10 ml of 0·1 *N* $AgNO_3$, and dilute to 50 to 60 ml. De-aerate the soln. with 1 to 2 g of $KHCO_3$, add excess of standard arsenite soln. and 2 drops of 0·01 *M* OsO_4, and after 1 to 2 min. titrate the excess of As_2O_3 with standard $Ce(SO_4)_2$ soln. The error may be as small as 0·1%.
R. E. ESSERY

2595. **Determination of perchlorates by fusion with nitrite.** E. Kurz, G. Kober and M. Berl (Central Lab., Military Ind. and Sci. Dept., Min. Defence, Tel-Aviv, Israel). *Anal. Chem.*, 1958, **30** (12), 1983–1986.—When fused with $NaNO_2$, ClO_4^- react to give Cl^-, which can be titrated. For 0·1 to 0·15 g of ClO_4^-, 1 g of $NaNO_2$ is required, or more if organic matter or metal powders are present. Surround a weighed sample with 1 g of $NaNO_2$ in a nickel crucible, cover and heat for 1·5 hr. at 500° ± 20°. Cool and dissolve the contents in 40 to 50 ml of hot H_2O. Titrate potentiometrically with 0·1 *N* $AgNO_3$, adding 0·04-ml increments near the end-point. Use a silver - silver chloride electrode and an external S.C.E. connected via a KNO_3 bridge. For titration with ferric alum as indicator, first destroy the excess of NO_2^- with 6 *N* HNO_3 and saturated $KMnO_4$, then add excess of 0·1 *N* $AgNO_3$ and back-titrate with 0·1 *N* KSCN. Alternatively, add excess of $AgNO_3$ soln., boil with HNO_3 and filter, then back-titrate the filtrate with 0·1 *N* KSCN.
P. D. PARR-RICHARD

2596. **The coulometric titration of bromate with cuprous copper.** G. M. Arcand (Dept. of Chem., Univ. of Missouri, Columbia, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 267–271 (in English).—The titration of bromine with electrolytically generated Cu^+ devised by Buck and Swift (*Anal. Chem.*, 1952, **24**, 499) has been applied to the titration of bromate. The soln. for titration contains 10 ml of 5 *N* NaBr, 1 ml of 0·5 *N* $CuSO_4$, 5 ml of 3 *N* $HClO_4$ and 35 ml of H_2O. After generation by electrolysis of a little bromine to destroy reducing agents, the polarity of the electrodes is reversed and Cu^+ are generated until the excess of bromine is destroyed. The bromate soln. (18 to 250 μg of $KBrO_3$) is then added and the titration completed. A precision of ± 0·3 μg is claimed.
T. R. ANDREW

2597. **Polarographic determination of iodate in liquid ammonium nitrate - ammonia.** W. Hubicki and J. Matysik (Inst. f. anorg. Chem., Univ. M. Curie-Skłodowska, Lublin, Poland). *Ann. Univ. M. Curie-Skłodowska, AA*, 1956, **11** (5), 39–45 (in German).—In liquid NH_4NO_3 - $2NH_3$ (Divers' liquid), iodate gives a well-defined polarographic wave at $E_{\frac{1}{2}} = -0{\cdot}75$ V *vs.* a mercury-pool electrode. By using Tl^- as an internal standard it is shown that the valency change for IO_3^- under these conditions is 5, indicating a reaction—

$$2IO_3^- + 12NH_4^+ + 10e \rightarrow I_2 + 12NH_3 + 6H_2O.$$

Periodate gives a wave at $E_{\frac{1}{2}} = -0{\cdot}04$ V.
T. R. ANDREW

2598. **Chemical studies of the sea. LXXV. Determination of manganese in seaweed.** Masayoshi Ishibashi and Toshio Yamamoto (Kyoto Gakugei Univ., Fushimi-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (10), 1184–1187.—The dissolution of sodium bismuthate in acid in the presence of Ag^+ (Kiyota and Yamamoto, *Anal. Abstr.*, 1957, **4**, 2976) is facilitated if the reagent is prepared by melting Na_2O_2, NaOH and $Bi(OH)_3NO_3$, and drying at > 105°. The decolorisation of Ag_2O_2 proceeds rapidly in the presence of urea. Chloride ions are masked with Hg^{2+}. The sample ash (0·25 g) is evaporated with conc. HCl and HNO_3 (a few drops each) and extracted with 3·6 *N* H_2SO_4 (20 ml). The product is treated with $HgSO_4$ (15% in 3·6 *N* H_2SO_4; 0·5 ml), Na_2BiO_3 (0·05 g) and $AgNO_3$ soln. (10%, a few drops), then heated at < 40°, mixed with urea (0·02 g) and diluted to 25 ml for colorimetry.
K. SAITO

2599. **Determination of alkalis in manufactured manganese dioxide.** Z. Řezáč and M. Adamec (Spolek Pro Chem. a Hutní Výrobu, Ústí nad

Labem, Czechoslovakia). *Chem. Listy*, 1958, **52** (10), 2006–2007.—If MnO_2 is reduced to the bivalent state, any alkalis adsorbed on the MnO_2 can be eluted with H_2O and determined by acidimetric titration. Finely powdered carbon is used for the reduction. *Procedure*—Mix the sample (1 g) in a platinum crucible with powdered carbon (1·5 g), cover with a layer of the same reducing agent (0·5 g) and heat for 10 min. at 800° in an electric furnace. Cool, place the crucible in a 250-ml beaker, add H_2O (100 ml), heat for 10 min., remove and wash the crucible, and transfer the liquid with the ppt. to a 500-ml flask and dilute to vol. with H_2O. Mix and set aside for 10 min. Measure a 50-ml aliquot by means of a pipette fitted with a filtration device (to remove any turbidity), into a 250-ml flask, add Tashiro indicator (5 drops) and titrate with 0·1 *N* HCl. Heat the soln. when approaching the end-point. The results are in good agreement with those obtained when the reduction is carried out with hydrogen. J. ZÝKA

2600. **Gravimetric determination of iron with benzenephosphinic acid.** J. E. Banks (Technol. Univ., Delft, Netherlands). *Anal. Chim. Acta*, 1958, **19** (4), 331–333.—The limitations of the macro-method in which the same reagent is used (*cf. Anal. Abstr.*, 1957, **4**, 2195) are overcome by working on a micro scale with soln. containing $\simeq$ 1 mg of Fe^{3+} per ml. *Procedure*—Warm 2 ml of the soln. of Fe^{3+} to 50° and neutralise to methyl orange with 4 *N* aq. NH_3. Add 1 ml of 2 *N* H_2SO_4 and dilute to 4 ml. Heat to 95° and add, dropwise with stirring, 1 ml of 0·2 *N* benzenephosphinic acid. Digest at 70° to 80° for 30 min. and cool in a refrigerator for 30 min. Collect the ppt. on a filter-stick and wash it with ice-cold water until the washings are free from SO_4^{2-}. Dry at 100° to 110°. Examination with the thermobalance shows that $Fe(C_6H_6PO_2)_3$ is stable up to 275°. H. N. S.

2601. **pH adjustment in colorimetric iron determinations.** N. F. Davis, C. E. Osborne, jun., and H. A. Nash (Pitman-Moore Co., Indianapolis, Ind.). *Anal. Chem.*, 1958, **30** (12), 2035.—If 2:2′-dipyridyl or 1:10-phenanthroline is used to determine Fe colorimetrically, adjustment of the pH before addition of the colour-forming reagent gives low results, owing to the pptn. of $Fe(OH)_2$ or $Fe(OH)_3$. The correct order of reagent addition is—reducing agent, colour-forming agent, buffer and finally base if necessary. P. D. PARR-RICHARD

2602. **Spectrophotometric constants in glacial acetic acid of 2:2′-dipyridyl and its 4:4′-disubstituted derivatives as iron(II) complex cations.** W. M. Banick, jun., and G. F. Smith (Noyes Chem. Lab., Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 304–306 (in English).—The ferrous complexes of 2:2′-dipyridyl and 11 4:4′-disubstituted 2:2′-dipyridyls were studied in glacial acetic acid (quinol added as reductant). In only two cases was the wavelength of maximum absorption changed more than 5 mμ from that in aq. soln. (*cf. Anal. Chim. Acta*, 1958, **18**, 269). The molar absorption values, except in two instances, were also comparable with those for aq. soln.
T. R. ANDREW

2603. **Amperometric titration of iron by means of EDTA (disodium salt) in various materials [ores, slags and minerals].** Yu. I. Usatenko and M. A. Vitkina (F. É. Dzerzhinskiĭ Dniepropetrovsk Chem. Tech. Inst.). *Zavod. Lab.*, 1958, **24** (9), 1058–1059.—On a rotating platinum anode EDTA is oxidised in both acid and alkaline soln. At pH 1 the wave height is four times that with neutral soln. In alkaline soln. the height increases with the content of alkali. The waves occur between 0·8 and 1·0 V and between 0·45 and 0·65 V *vs.* the S.C.E. To determine Fe in iron ore, the sample (0·1 g) is dissolved in HCl with addition of HNO_3. Ores insol. in acid are decomposed by fusion with Na_2CO_3, followed by treatment with dil. HCl. The soln. after evaporation to a small vol. and dilution with water is treated with KNO_2 and neutralised by means of aq. NH_3 and dil. HCl so that it is left slightly acid with an excess of 1 to 2 drops of dil. HCl (1:1). After the soln. has been diluted to $\simeq$ 50 ml, a platinum micro-electrode is inserted, connection is made to a S.C.E., an e.m.f. of + 0·9 V is applied and the stirred soln. is titrated with 0·05 *M* EDTA. G. S. SMITH

2604. **Phthalocyanines as oxidation - reduction indicators. IV. Use of copper phthalocyaninetetrasulphonic acid (Cu - PTS). Titration of iron(II), ferrocyanide and uranium(IV) with permanganate.** G. Gopala Rao and T. P. Sastri. *Z. anal. Chem.*, 1958, **163** (4), 266–272 (in English).—Experimental conditions for these titrations were investigated. With copper phthalocyaninetetrasulphonic acid (**I**) as internal indicator, cobalt and nickel salts (up to 1 g in 100 ml) do not interfere in the titration of Fe^{II} with $KMnO_4$. The use of **I** in the titration of Fe^{II} in HCl medium and in the presence of 1 ml of 0·05 *M* $MnSO_4$ is shown to eliminate entirely interference due to HCl. For the titration of U^{IV}, an aliquot is diluted to 100 ml with *N* H_2SO_4, 3 ml of syrupy H_3PO_4 and 2 drops of **I** are added, and the mixture is titrated with 0·01 *N* $KMnO_4$.
B. B. BAUMINGER

2605. **Contributions to the determination of iron and aluminium in a mixture.** A. Todeasa, D. Ciolan, A. Kovacs and C. Turcanu (Fac. Pharm., Univ. Cluj). *Rev. Chim., Bucharest*, 1958, **9** (10), 577–578.—The method is based on the pptn. of Fe with NaOH and pptn. of Al from the filtrate with ammonium benzoate. *Procedure*—A mixture of $FeCl_2$ and $AlCl_3$ in $\simeq$ 150 ml of water is boiled and treated with excess of 2 *N* NaOH. The ppt. is washed four or five times with boiling water, then purified by dissolving in HCl and re-pptg. with aq. NH_3, washing the ppt. with boiling water till free from Cl^-, and calcining to Fe_2O_3. The filtrate containing the Al is acidified to methyl red with HCl to pH 5 to 5·5, and the Al is pptd. in the warm with 30 to 40 ml of 5% Na benzoate soln. The ppt. is allowed to stand on the water bath for 10 to 15 min., then filtered off immediately and washed with a boiling mixture of 5 ml of 5% ammonium benzoate soln. and 1 ml of conc. acetic acid per 100 ml until free from Cl^-. It is then ignited to Al_2O_3. The error is − 0·08 to − 0·76% for Fe and − 0·6 to + 0·40% for Al. H. SHER

2606. **Complexometric determination of iron and aluminium in iron - aluminium bronze.** M. I. Rozenberg (Odessa Road Chem. Tech. Lab.). *Zavod. Lab.*, 1958, **24** (9), 1060.—The sample (1 g) of bronze is dissolved in 15 ml of dil. HNO_3 (2:1), 90 ml of water is added, and Cu is removed by electrolysis. Portions (3 × 10 ml) of the diluted electrolyte (250 ml) are separately diluted to 90 ml and, after being heated to between 50° and 60° and mixed with 2 ml of a soln. prepared by dissolving 10 g of sulphosalicylic acid in 65 ml of water and

adding 35 ml of 2 *N* NaOH, are then titrated with 0·05 *N* EDTA (disodium salt) until the pink colour is discharged, to give the content of Fe. The titrated soln. is treated with the titrant in excess such that the back-titration with a soln. of Fe, prepared by dissolving 4·8 g of $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ in one litre of water containing 2 ml of H_2SO_4, will comprise between 5 and 9 ml. The soln. at 70° is neutralised with an ammoniacal buffer soln. to methyl red indicator, boiled, cooled, mixed with 10 ml of an acetate buffer soln. (pH 6), and titrated with the soln. of Fe to give the content of Al. G. S. SMITH

2607. **Indirect polarographic and complexometric determination of very small amounts of arsenic in iron and ores.** A. Černý (Chem. Lab. VŽKG, Ostrava, Czechoslovakia). *Hutn. Listy*, 1958, **13** (8), 715–716.—After distillation from the sample, As is pptd. as As_2S_3, converted with aq. NH_3 into $(NH_4)_3AsS_3$ and treated with a known excess of $CdSO_4$ soln. The pptd. CdS is separated and the excess of Cd^{2+} is determined polarographically in aq. NH_3 medium, or complexometrically in aq. NH_3 - NH_4Cl buffer soln. (pH 10), with EDTA (disodium salt) soln., with Eriochrome black T as indicator. When titrating complexometrically, the ppt. of CdS need not be separated from the soln. J. ZÝKA

2608. **Bromatometric analyses. IV. Volumetric determination of ferrocyanide ions with standard potassium bromate solution.** E. Sugár and L. Szekeres (Agric. Chem. Inst., Univ. Budapest, Hungary). *Z. anal. Chem.*, 1958, **163** (4), 250–252.—The titration of $Fe(CN)_6^{4-}$ is carried out in dil. HCl medium with 0·1 *N* $KBrO_3$, with iodised starch as indicator. This method has been checked by titration with ceric sulphate, with ferroin as indicator. Results of both methods show good agreement. B. B. BAUMINGER

2609. **Potentiometric determination of potassium ferricyanide.** R. S. Saxena and C. S. Bhatnagar (Gov. Coll., Kota, Rajasthan, India). *Anal. Chim. Acta*, 1958, **19** (4), 402–405.—Solutions of $K_3Fe(CN)_6$ (0·001 *M* to 0·25 *M*) and $AgNO_3$ (0·004 *M* to 0·4 *M*) are titrated against each other in both directions. The end-point is detected potentiometrically with the use of a silver-plated platinum-gauze electrode and a S.C.E. with a saturated KNO_3 bridge. The reaction involves the formation and pptn. of $Ag_3Fe(CN)_6$. The addition of 20% of ethanol or 1 g of NH_4NO_3 has little effect on the accuracy of the end-point. H. N. S.

2610. **Determination of trace amounts of aluminium in cast iron.** R. C. Rooney (The British Cast Iron Res. Assoc., Bordesley Hall, Alvechurch, Birmingham, England). *Analyst*, 1958, **83**, 546–554.—The soln. of the sample in a known vol. of cold dil. HCl is centrifuged. An aliquot of the supernatant liquid is treated with acetic acid, Na acetate and aq. Na diethyldithiocarbamate soln. and extracted with $CHCl_3$, according to a specified procedure, to remove major constituents; the extracts are discarded. The aq. layer is treated with aq. cupferron soln. and extracted with $CHCl_3$ and the extract is evaporated to dryness. The residue is fumed with HNO_3 and $HClO_4$, HCl being included if it is necessary to volatilise Cr as CrO_2Cl_2. If the $CHCl_3$ extract is colourless or pale green the residue is dissolved in $HClO_4$, Na acetate soln. and Solochrome violet RS soln. are added and, after adjustment of the vol., the Al is determined polarographically. If the $CHCl_3$ extract is yellow or brown (owing to the presence of Ti or Fe) the soln. of the dry residue in $HClO_4$ is treated with cupferron soln. and washed with $CHCl_3$ until colourless. After adjustment of the pH, the Al is extracted and determined as before. Modified procedures for the initial treatment of the sample are described for plain cast iron containing 0·0004 to 0·004%, cast iron containing 0·0004%, or alloy cast iron containing 0·0005% of Al, and for the determination of acid-insol. Al. A. O. JONES

2611. **Determination of carbon and its distribution in iron by a radiation method.** L. Šimon. *Hutn. Listy*, 1958, **13** (8), 708–711.—Various methods are evaluated; autoradiography is the most convenient. J. ZÝKA

2612. **Recent developments in NBS spectrographic standard samples of iron-base alloys.** R. E. Michaelis (National Bureau of Standards, Washington, D.C.). *Appl. Spectroscopy*, 1958, **12** (4), 114–116.—A list of compositions of eight new ingot iron and low-alloy steel standards is given. These cover 17 elements, including carbon and phosphorus. Compositions of two groups of stainless-steel standards are given and one of these groups, comprising six alloys, together with a further group of six tool-steel standards, has been made available as discs, 1·25 in. diam. by 0·25 in. thick, suitable for X-ray fluorescence spectroscopy. P. T. BEALE

2613. **Spectrographic determination of boron and silicon in low-alloy steel by fluoride evolution.** J. E. Paterson and W. F. Grimes (Graham Res. Lab., Jones and Laughlin Steel Corp., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1900–1902.—The sample is charged with copper fluoride which decomposes when heated by relatively low current arcs to provide labile F which will combine with B and Si to form volatile fluorides. The fluorides can be distilled from deep-cratered electrodes preferentially to most other compounds and produce a spectrum consisting mainly of B and Si lines. In the concn. range 0·001 to 0·02%, the coeff. of variation is ± 3·0% for B and ± 3·2% for Si. K. A. PROCTOR

2614. **Volumetric determination of silicon in steel.** M. Habrcetl and M. Habrcetlová (Železárny Čenkov, Czechoslovakia). *Hutn. Listy*, 1958, **13** (8), 721–722.—Silicon is converted into ammonium fluorosilicate, separated as K_2SiF_6 and determined volumetrically with NaOH soln.; HF, used in previous procedures of this type, is replaced by NH_4F. *Procedure*—Dissolve the sample (1·5 to 2 g) in HNO_3 (1:1) (35 to 40 ml), heat till the vol. is reduced to 10 ml, cool and transfer to a 100-ml plastic vessel. Add NH_4F (3 g), mix, set aside for 3 min., add KNO_3 (12 g) and set aside for 10 to 15 min. with occasional stirring. Filter through a paper filter, wash the ppt. with KNO_3 soln. (20%) till the filtrate becomes red after addition of 2 drops of 0·1 *N* NaOH and of phenolphthalein. Transfer the filter to a titration vessel, add H_2O (100 ml) (at 80°), mix and titrate with 0·1 *N* NaOH (phenolphthalein indicator). The factor for the NaOH soln. must be determined with a sample of steel containing a known amount of Si. J. ZÝKA

2615. **Determination of nickel by a solvent-extraction method.** P. D. Blundy and M. P. Simpson (Chem. Engng Div., A.E.R.E., Harwell,

Berks., England). *Analyst*, 1958, **83**, 558–561.—In the method described, Ni is determined in soln. containing U, Th, Cu, Fe and Cr. In the presence of Th, Fe and Cr, an aliquot of the soln. (≡ 5 to 100 μg of Ni) is treated with enough 20% tartaric acid soln. to prevent hydrolysis of thorium salts. Sodium acetate is added and the pH is adjusted to 5 to 5·5 with 2 *N* NaOH. The liquid is then extracted with a 0·1% w/v aq. soln. of 4-methyl-*cyclo*hexane-1:2-dione dioxime and the nickel complex is extracted with a known vol. of toluene. The extinction of the toluene extract is measured in a Spekker absorptiometer with H556 filters (365 mμ) and a mercury-vapour lamp. In the presence of U, Cu, Fe and Cr, an aliquot (≡ 5 to 200 μg) is treated with 1 ml of tartaric acid soln., 1 ml of 10% v/v thioglycollic acid soln. and 1 ml of 10% w/v Na acetate soln. The pH is adjusted to 5 to 5·5 with 2 *N* NaOH and the procedure is then as before. The calibration graph is prepared by the same procedures. The mean recovery for several determinations was 98% and the standard deviation ± 1·2%. A. O. JONES

2616. **S-Substituted thioureas as analytical reagents. III. S-Methylthiourea sulphate as a colorimetric reagent for nickel and cobalt.** S. K. Siddhanta and S. N. Banerjee (Applied Chem. Dept., Indian Inst. of Technol., Kharagpur). *J. Indian Chem. Soc.*, 1958, **35** (8), 547–552.—S-Methylthiourea sulphate is used as a colorimetric reagent for Co and Ni in ammoniacal medium. The colour formed is deep enough to make the reagent sensitive. Beer's law is obeyed. The effects of variation of the ageing period, the pH of the medium and the amount of the reagent are studied, and suitable filters are indicated. I. JONES

2617. **Photometric determination of nickel in the presence of large amounts of copper.** Sheau-Wei Kwauk (Anshan Branch Lab., Bureau of Geology, Min. of Metallurg. Ind.). *Acta Chim. Sinica*, 1958, **24** (5), 352–355.—Nickel can be determined in the presence of > 1000 times its wt. of Cu (*e.g.*, in copper ores) by addition of EDTA after the colour complexes of Cu and Ni with dimethylglyoxime have been developed. The copper complex is destroyed while that of Ni is unchanged; in strong alkali, the copper complex is not completely removed. The recovery is good for 10-μg amounts of Ni added to > 10 mg of Cu. (From English summary.) S.C.I. ABSTR.

2618. **X-ray spectrographic analysis of nickel-containing alloys with varied sample forms.** C. M. Davis and G. R. Clark (International Nickel Co. Inc., Bayonne, N.J., U.S.A.). *Appl. Spectroscopy*, 1958, **12** (4), 123–126.—Quantitative analysis of drillings, wire or odd-shaped pieces of sample may be obtained by dissolving them in acid and converting them into oxides. These may then be mounted directly on to microscope slides with a drop of lacquer or mixed with an equal weight of graphite and pressed into pellets. The method permits the use of synthetic standards when chemically analysed ones are not available. Typical results are shown for the determination of Zn, Ni, Sn and Cu in a bronze by the first method, and for W, Mo and Nb in a high-temperature Ni-base alloy by the second. The average deviation between chemical and X-ray fluorescence results is of the order of ± 0·05 at the 5% content level, except for Sn in the Cu-base alloy, when differences range from − 0·42 to + 0·30. P. T. BEALE

2619. **Electro-analysis of cobalt, nickel and copper in plutonium solutions with a mercury cathode.** K. S. Bergstresser (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-1064, Feb. 3, 1950. Decl. Aug. 30, 1956. 22 pp.—Equipment and analytical procedure are described for the determination of Co, Ni or Cu in the presence of Pu by electro-deposition on a mercury cathode. Only sub-microgram quantities of Pu remain with the amalgam which is formed. The analyses of some binary plutonium alloys of these metals are reported. NUCL. SCI. ABSTR.

2620. **Determination of cobalt, nickel and copper in the presence of plutonium.** K. S. Bergstresser (Los Alamos Sci. Lab., N. Mex.). *U.S. Atomic Energy Comm.*, Rep. LA-1063, Feb. 13, 1950. Decl. Aug. 30, 1956. 38 pp.—Procedures for the analysis of plutonium binary alloys of cobalt, nickel and copper were developed. They include colorimetric determination of Co with nitroso-R salt and of Ni with dimethylglyoxime. Satisfactory gravimetric procedures have involved pptn. of Cu with salicylaldoxime and as cuprous thiocyanate, and pptn. of Ni with dimethylglyoxime. One volumetric method, copper by iodimetric titration, was also used. The recommended methods were employed in the analysis of various plutonium alloys. NUCL. SCI. ABSTR.

2621. **Spectrophotometric determination of palladium. I. Bismuthiol I as an analytical reagent.** A. K. Majumdar and M. M. Chakrabartty (Jadavpur Univ., Calcutta). *Anal. Chim. Acta*, 1958, **19** (4), 372–376.—A spectrophotometric method for Bi results from an investigation of the red colour the metal yields with bismuthiol I (2:5-dimercapto-1:3:4-thiadiazole). *Procedure*—Adjust the test soln., containing up to 10 μg of Pd^{2+}, to a pH value between 6 and 10, add 4 ml of a 0·25% soln. of bismuthiol I (0·25 g dissolved in the minimum vol. of *N* NaOH and diluted with water to 100 ml) and 2·5 ml of ethanol, and dilute to 25 ml. Measure the extinction at 400 mμ in a 1-cm cell and interpret the result from a calibration graph. Interference from other metals can be limited by adding 50 μg of EDTA, but Pt, Au, Cu, Cr, Fe, Hg, Ag, Tl, U, VO_3^- and CN^- must be absent. The complex has the formula $Pd(C_2N_4S_3)$ and a dissociation constant of $3{\cdot}2 \times 10^{-5}$ at 25°. H. N. S.

2622. **The use of ethylenediaminetetra-acetic acid or nitrilotriacetic acid as masking agents in the determination of palladium with dimethylglyoxime or quinaldic acid.** P. F. Lott, R. K. Vitek and K. L. Cheng (Univ. of Missouri, Rolla, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 323–327.—Several metals normally interfere in the pptn. of Pd with dimethylglyoxime, but pptn. in the presence of EDTA eliminates their disturbing effects. If Bi is present, tartrate must also be added. *Procedure*—To the soln. (200 ml), containing 15 to 150 mg of Pd, add sufficient 0·1 *M* EDTA (disodium salt) to complex other metals present, adjust to pH 5·5, heat to 60° to 70° and add dropwise a 20% excess of dimethylglyoxime soln. (0·01 *M* in ethanol or 0·1 *M* in acetone). Digest at 60° to 70° for 30 to 45 min., filter in a sintered glass crucible, wash the ppt. 3 to 5 times with 10-ml portions of 0·1 *N* HCl and then with water, and dry it at 125°. The complex contains 31·67% of Pd. Pptn. with quinaldic acid is preferred since this reagent is water-soluble and the ppt. is more readily collected, but nitrilotriacetic acid must then be used in place

of EDTA, the procedure being otherwise the same. The quinaldate contains 23·66% of Pd. The quinaldates of Fe, Cu and Zn are co-pptd. to a small extent, but are removed by washing with 0·1 *N* HCl. Both complexing agents reduce Au^{3+} to the metal. H. N. S.

See also Abstracts—**2455**, Analytical chemistry of fused media. **2457**, Dithio-oxamide derivatives as colorimetric reagents for metals. **2459**, Separation of alkaline-earth metals from other metals. **2460**, Separation of Bi, Pb and Cd from Hg, and of Bi and Hg from In. **2465**, Applications of the EDTA titration. **2624**, Determination of CO_2. **2703**, Colorimetric determination of P. **2792**, Determination of Cu, Pb and Zn in water and soil. **2798**, Determination of B in fertilisers. **2824**, Removal of heavy metals from ion-exchange resins.

3.—ORGANIC ANALYSIS

Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.

2623. **Microchemical organic reactions on glass-fibre paper.** V. Prey and A. Kabil (Inst. of Org. Chem., Tech. Coll., Vienna). *Öst. ChemZtg*, 1958, **59** (19–20), 260–262.—The use of glass-fibre paper for the analysis of organic compounds in paper chromatography is described. The sample (0·1 to 0·5 mg) and the reaction agent are placed on a circular glass-fibre paper of 3 cm in diam. For reactions at elevated temp., the use of a micro-autoclave (a cylindrical and electrically heated copper block) is recommended. The reaction products are eluted with suitable solvents by descending chromatography on to strips of glass-fibre paper. A technique is described for concentrating the eluted matter in a small area. The method has been tested for the following reactions—alcohols (primary and secondary aliphatic) with 5 *N* KOH and CS_2; alkyl halides with dry pyridine at elevated temp.; aldehydes and ketones with 2:4-dinitrophenylhydrazine; nitration of aromatic hydrocarbons with fuming HNO_3; tertiary amines with methyl iodide, etc. The micro-autoclave and elution apparatus are illustrated. B. B. BAUMINGER

2624. **Titrimetric determination of carbon dioxide, with special reference to the determination of carbon in organic compounds.** R. Belcher, J. H. Thompson and T. S. West (The Univ., Birmingham, England). *Anal. Chim. Acta*, 1958, **19** (4), 309–315.—The CO_2 from the combustion of organic substances is absorbed in $Ba(OH)_2$ soln. containing $BaCl_2$ [20% (w/v)] and the excess of $Ba(OH)_2$ is titrated with standard HCl in the presence of *o*-cresolphthalein as indicator. The method proves less accurate than the gravimetric method of CO_2 determination. H. N. S.

2625. **Rapid methods of micro-elementary analysis. XV. Simultaneous micro-determination of carbon, hydrogen and halogens in organic compounds.** M. O. Korshun, N. É. Gel'man and N. S. Sheveleva (Inst. of Elementary Organic Compounds, USSR, Moscow). *Zhur. Anal. Khim.*, 1958, **13** (6), 695–701.—An improved modification of the method for the simultaneous determination of C, H and halogen has been developed. The apparatus consists of a combustion tube and an inner quartz tube. Silvered pumice is used for absorption of halogens. The possibility of using this preparation at 425° has been shown and the absorption capacity of silver pptd. on pumice has been established as considerably higher than that of electrolytic silver. First carry out a "blank." Introduce the quartz tube with silver into the combustion tube and heat electrically the part of the tube containing silver, up to 575° when metallic silver is used and up to 425° when silvered pumice is used. Connect the absorbing apparatus and pass 500 ml of oxygen at 35 to 40 ml per min. When the "blank" combustion is completed, remove the absorbing apparatus from the electric oven and cool the inner quartz tube by passing oxygen for 5 to 8 min. Weigh the absorbing apparatus and the quartz tube and re-assemble them, and leave in an atmosphere of oxygen with the aspirator closed. Introduce a tube with a sample into the inner quartz tube and place both of them in the combustion tube. Combustion of completely halogenated hydrocarbons is carried out at 900° with electrical heating. The same technique is applied for the determination of H, C and S, but the combustion temp. should be 750°. W. ROUBO

2626. **Swift Dumas nitrogen estimation.** I. K. H. Otter (Chesterford Park Res. Sta., Fisons Pest Control, Ltd., nr. Saffron Walden, Essex). *Nature*, 1958, **182**, 656–657.—A new apparatus is described. The sample (3 to 7 mg) is placed in an inner tube, partly filled with copper oxide wire, and with an outlet to a source of CO_2. An outer, concentric tube, sealed at one end, is connected via a ground glass joint and 3-way tap to the nitrometer, and the annular space between the tubes is packed with CuO and copper wire. Combustion takes about 5 min. Results are given for dinitrobenzene and azobenzene. P. D. PARR-RICHARD

2627. **A routine flame-photometric determination of organic chloride.** G. E. Marsh (Res. Dept., Standard Oil Co., Whiting, Indiana, U.S.A.). *Appl. Spectroscopy*, 1958, **12** (4), 113–114.—Organically combined chlorine over the range 0·1 to 1·0% is determined by measurements of the copper chloride band at 436 mμ. Copper is added as copper octoate to all samples. The coeff. of variation is about 3% of the content, with good agreement between chemical and spectrographic results. P. T. BEALE

2628. **Quantitative organic analysis. XX. Micro-determination of chlorine in organic compounds by combustion in an empty tube.** M. Večeřa and J. Bulušek (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (8), 1526–1536.—The compound is heated to 720° in a stream of O in an empty tube (*cf. Anal. Abstr.*, 1958, **5**, 854), the Cl is absorbed in dil. H_2O_2 and the Cl^- are titrated with 0·01 *N* $AgNO_3$, with Brilliant yellow as adsorption indicator. Statistical evaluation of 79 results establishes the accuracy of the method. J. ZÝKA

2629. **Determination of chlorine in organic compounds with radium - beryllium neutron source by neutron absorption technique.** Yuzuru Kusaka (Fac. of Sci., Konan Univ., Higashinada-ku, Kobe).

J. Chem. Soc. Japan, Pure Chem. Sect., 1958, **79** (10), 1266–1267.—The neutron source (50 mg of Ra) is inserted in the sample soln. (in a hydrocarbon) (250 ml) placed in a paraffin wax vessel. The neutron flux is measured by the activation of In (^{116m}In). The degree of neutron absorption is proportional to the amount of Cl for $<$ 10 g per 100 ml. K. SAITO

2630. **Quantitative determination of halogens in organic substances. III. Simultaneous separate gravimetric determinations of chlorine, bromine and iodine with respect to two or three of these elements in a single sample.** P. N. Fedoseev and M. Ya. Sobko (S. O. Makarov Nikolayev Shipbuilding Inst., USSR). *Zhur. Anal. Khim.*, 1958, **13** (6), 702–705.—The method is based on the mutual displacement of halogens from metal bromides and iodides when heated. For quant. determinations, KBr and NaBr must be heated up to 680° to 720°, and KI up to 480° to 520°. The apparatus is simple, and consists principally of a combustion tube heated by two electric furnaces (first 750° to 800°, second 800° to 900°) and connected in series with two absorption tubes (the first heated at 680° to 720° and filled with KBr; the second heated at 480° to 520° and filled with KI). Beyond these absorption tubes there is a short tube containing 2 to 3 g of moist KI joined finally to a spiral tube containing 10% KI soln. Weigh and connect the absorption tubes and heat them to the required temperature. Cover the weighed sample in a boat with powdered silica sand or chromium oxide, and place it in the combustion tube. Pass oxygen through the system at 150 to 250 ml per min. and when combustion is complete (in 10 to 30 min.) heat the whole length of the combustion tube for another 5 to 10 min., then remove and weigh the absorption tubes. Transfer the contents of the absorption tubes containing KI to a flask and titrate the iodine with 0·05 *N* $Na_2S_2O_3$. Equations are given for calculating the individual halogens. The experimental error is within 0·1 to 0·2%. A single analysis takes 50 to 60 min. W. ROUBO

2631. **Sub-micro methods for the analysis of organic compounds. IV. The determination of iodine and bromine.** R. Belcher, R. A. Shah and T. S. West (Chem. Dept., Univ. Birmingham, England). *J. Chem. Soc.*, 1958, 2998–3002.—A sodium-fusion method is used to determine iodine or bromine in 50-μg samples with an accuracy within $\pm$ 0·4% (absolute). *Procedure for iodine*—Weigh the sample into a fusion tube of borosilicate glass, add a 7-mm length of 1-mm sodium wire, seal, and heat at 350° for 15 min. Open the tube and add H_2O (0·2 ml). Filter through paper pulp after 2 min., and wash the filter with H_2O (about 1·5 ml used in small portions). Neutralise the combined filtrate and washings to methyl red with 2 *N* H_2SO_4, add bromine water (2 drops) and after 30 sec. add 90% formic acid (2 drops). Stir magnetically for 7 min., remove fumes of Br, add 2 *N* H_2SO_4 (1 drop) and 10% KI soln. (3 drops) and titrate with 0·01 *N* $Na_2S_2O_3$, with Thyodene as indicator. Perform a blank titration. To determine iodine in nitrogenous compounds, boil the filtrate and washings with a slight excess of acetic acid before the oxidation with Br. *Procedure for bromine*—Perform the fusion and extraction as above. Neutralise the filtrate and washings to methyl red with 2 *N* HCl, add *N* NaOCl soln. (0·3 ml) and sufficient NaH_2PO_4 soln. to give a pH of 6·2. Heat at 94° for 15 min., add 50% Na formate soln. (3 drops) and allow to cool. Stir the soln. with 12 *N* H_2SO_4 (6 drops), 10% KI soln. (3 drops) and 2·9% ammonium molybdate catalyst soln. (1 micro drop) and titrate the liberated iodine. Perform a blank determination. A. R. ROGERS

2632. **Rapid method for the determination of iodine in organic substances.** W. Kirsten and S. Ehrlich-Rogozinsky (Inst. of Med. Chem., Univ. of Uppsala, Sweden). *Chemist Analyst*, 1958, **47** (3), 58–59.—The sample (4 to 5 mg for micro-, 10 to 15 mg for semi-micro determination) is placed in a flask which is fitted with a special absorption-head containing 1 ml of acetate buffer (pH 4·5), 2 ml of water and 2 ml of 5% NaOCl soln. To the flask is added 1·5 ml of an oxidation mixture (20 ml of conc. HNO_3, 30 ml of 72% $HClO_4$ and 5 ml of conc. H_2SO_4), the absorption-head is attached at once and the flask is heated till the $HClO_4$ fumes, and for 3 to 5 min. longer. The contents of the absorption-head are diluted to 50 ml, treated with 5 ml of phosphate buffer (90 g of $NaH_2PO_4.2H_2O$ in 180 ml of water), boiled for 5 min. to expel Cl, and cooled. Sodium iodide soln. (5 ml of 10%) is added, and the liberated iodine is titrated with 0·05 or 0·01 *N* thiosulphate, with starch as indicator. Some elements, *e.g.*, Cu and V, interfere. Mean results for 10 compounds show good agreement with the theoretical, and satisfactory precision. R. E. ESSERY

2633. **Highly sensitive determination of sulphur and simultaneous determination of carbon and sulphur with a recording conductivity meter.** W. Koch, S. Eckhard and H. Malissa (Max Planck Inst. für Eisenforschung). *Arch. Eisenhüttenw.*, 1958, **29** (9), 543–546.—The apparatus described previously (*cf.* Koch and Malissa, *Arch. Eisenhüttenw.*, 1956, **27**, 695) for the determination of carbon has been modified for use in the determination of sulphur. Best results were obtained with 0·004 *N* $TlCl_3$ adjusted to a pH of 3 with HCl. Relative merits of connections in parallel and in series for the simultaneous determination of carbon and sulphur are discussed. H. SAWISTOWSKI

2634. **Detection of sulphur-containing compounds by paper chromatography.** L. Jirousek (Res. Inst. Endocrinol., Prague). *Chem. Listy*, 1958, **52** (8), 1553–1559.—A new method is described in which the compounds (about 100) are chromatographed on paper. The paper is passed through a freshly prepared 3% soln. of sodium in liquid ammonia, which reduces the compounds to thiols. The chromatogram is dried and moistened with 2% sodium nitroprusside soln., by which the spots are detected. J. ZÝKA

2635. **Determination of phenolic hydroxyl by near-infra-red spectrophotometry.** R. F. Goddu (Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2009–2013.—The use of the 2·7 to 3·0-μ region for qual. and quant. analysis of individual phenols and their mixtures, and the effect of substitution and intramolecular hydrogen bonding on the free-hydroxyl stretching band, are described. The molar absorptivity of most phenols is $\simeq$ 200 litres per mole-cm and this allows analysis of samples containing as little as 25 p.p.m. of phenolic hydroxyl. Because intramolecular hydrogen bonding causes shifts in the hydroxyl band it is possible to analyse some phenolic mixtures. All

other free-hydroxyl-containing compounds absorb and may interfere. Data for $\simeq 40$ phenols and polyhydric phenols are listed. G. P. Cook

2636. **Determination of terminal epoxides by near-infra-red spectrophotometry.** R. F. Goddu and D. A. Delker (Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2013–2016.—Terminal epoxides have sharp absorption bands at 1·65 and 2·20 μ. These bands are useful for the determination of epoxides in a variety of mixtures. Both terminal epoxides and terminal olefins may be simultaneously determined in the same sample. Other oxygen rings do not interfere. The accuracy and precision are $\pm$ 1 to 2% of the amount present, by direct determination in CCl_4. The limit of detection is $\simeq$ 10 μg per ml. G. P. Cook

2637. **Determination of oxirane oxygen in salts of epoxy acids and in the presence of amines.** A. J. Durbetaki (Food Machinery and Chem. Corp., Buffalo, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2024–2025.—Two methods are described and both are based on the fact that addition of an epoxy salt to acetic acid results in the regeneration of the epoxy acid and the formation of the metal or amine acetate. Titration of this soln. with HBr in acetic acid gives the corresponding bromohydrin and the metal or amine hydrobromide. In the first procedure the HBr consumed is determined by titration with 0·1 *N* $AgNO_3$, and in the second the metal or amine acetate is instantly regenerated by addition of excess of mercuric acetate followed by titration with 0·1 *N* $HClO_4$ in acetic acid. Eosin Y and crystal violet are used as indicators for the first and second methods, respectively. Recoveries are > 98·5%. G. P. Cook

2638. **A study of silver nitrate solutions in gas chromatography.** M. E. Bednas and D. S. Russell (Div. Appl. Chem., Nat. Res. Council of Canada, Ottawa). *Canad. J. Chem.*, 1958, **36** (9), 1272–1276.—A satd. soln. of $AgNO_3$ in either ethanediol or glycerol is an effective medium for the gas-chromatographic separation of olefins. Soln. in polyethylene glycol are considerably less effective. Separations of *cis*- and *trans*-but-2-ene and of but-1-ene and *iso*butene were very satisfactory. N. E.

2639. **Determination of the metal content of alkyl metal carbonates.** V. I. Kurov. *Vestn. Leningr. Univ.*, 1958, No. 10, *Ser. Fiz. i Khim.*, (2), 139–142.—The analysis of compounds of the types $RMCO_3$ and $R_2M(CO_3)_2$, where R is an alkyl radical and M is an alkali or an alkaline-earth metal, is studied. It is shown that addition of an excess of 0·1 *N* HCl to the sample (0·1 to 0·2 g), followed by back-titration with 0·1 *N* NaOH in the presence of methyl orange indicator, is satisfactory. G. S. Smith

2640. **Ammonium molybdate as spraying agent for paper chromatograms of reducing sugars.** H. El Khadem and S. Hanessian (Chem. Dept., Alexandria Univ., Egypt). *Anal. Chem.*, 1958, **30** (12), 1965.—After development and drying of sugar chromatograms the paper is sprayed with 10% ammonium molybdate soln. and heated to 100° for 10 min. The spots are at first yellow, but after about 6 hr. become blue-grey on a colourless background. There is no fading, nor does the background discolour provided that the paper is not exposed to strong light. H. F. W. Kirkpatrick

2641. **Determination of reducing sugars and reducing end-groups in polysaccharides by reaction with C-14-labelled cyanide.** J. D. Moyer and H. S. Isbell (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1975–1978.—Reaction of the sugar with the cyanide reagent is carried out in sealed tubes at 50° to 55° for 24 hr. Excess of cyanide is removed by volatilisation and the radioactivity of the residue is measured. The method is suitable for the determination of from 0·0001 to 0·001 millimole of reducing sugars. H. F. W. Kirkpatrick

2642. **Improved N-ethylcarbazole determination of carbohydrates with emphasis on sea-water samples.** Z. P. Zein-Eldin and B. Z. May (U.S. Fish and Wildlife Service, Galveston, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1935–1941.—The determination was examined with regard to heating time, method of reagent addition, concn. and precision. The reaction of the reagent with various sugars was also studied under revised conditions. The sensitivity was increased by more than three-fold with the modifications recommended; 3 μg of total carbohydrate per sample (1 mg per litre) was accurately determined. G. P. Cook

2643. **Determination of the acidity of cellulose.** H. Stübchen-Kirchner (Inst. für die Chemie und chem. Technol. des Papiers und Zellstoffes der Tech. Hochschule, Graz). *Öst. ChemZtg*, 1958, **59** (15–18), 226–234.—The causes of acidity in cellulose are discussed, and methods of determination of carboxyl groups are reviewed. These include decarboxylation, spectroscopic methods, and double decomposition. This last method comprises titration of acidity as such, titration of the acid liberated from a metal salt, and estimation of a combined cation, which may be a metal ion or a dyestuff ion. Liberation of the free carboxyl groups by demineralisation with various reagents, including dil. HCl and CO_2, and electrodialysis is described, and it is stated that the use of radioactive HCl has shown that no trace of reagent acid remains after only three washings. H. M.

2644. **Determination of water by the Karl Fischer method. Part 4. Determination of water in ketones.** British Standards Inst. (2 Park St., London). Addendum No. 1 (1959) to B.S. 2511: 1954, 4 pp.—Apparatus and procedures are specified for the determination of water in ketones by two methods; in one a modified Karl Fischer reagent is used which gives enhanced precision at very low water contents, and in the other methanol and pyridine are added to the reaction vessel. A single-burette method with electrometric end-point is also given. R. E. Essery

2645. **Polarographic determination of semicarbazones.** D. M. Coulson (Dept. of Chem., Stanford Res. Inst., Menlo Park, Calif.). *Anal. Chim. Acta*, 1958, **19** (3), 284–292 (in English).—The semicarbazones of acetone ($E_{\frac{1}{2}}$ = — 1·3 V *vs.* the S.C.E.), *iso*butyl methyl ketone (— 1·3 V), acetaldehyde (— 1·16 V), formaldehyde (— 1·05 V), *cyclo*hexanone (— 1·2 V), butyraldehyde (— 1·11 V), crotonaldehyde (— 1·06 V) and acraldehyde (— 0·99 V) give satisfactory polarographic waves at pH 4·6 in a basal soln. 0·1 *M* in acetic acid, Na acetate, NaCl and semicarbazide, and 0·0016% in Triton X-100. The diffusion current constant was approx. 7 (except for *iso*butyl methyl ketone when it was 4),

so that the total diffusion current at − 1·4 V may be used as a measure of total carbonyl compounds. The procedure has been used for the examination and determination of carbonyl compounds in air. Draw the sample through a liquid scrubber containing the polarographic basal soln. and record the polarogram. The optimum concn. range of semicarbazone is 10^{-5} to 10^{-4} *M*. T. R. ANDREW

2646. **Chemical analysis by measurement of reaction rates. Determination of acetylacetone.** W. J. Blaedel and P. L. Petitjean (Univ. Wis., Madison, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1958–1965.—Known weights of the sample are treated with a standard reagent soln., the reaction being one that results in a change of conductance. The progress of the reaction can then be followed instrumentally, in this instance with a high-frequency apparatus. The technique was applied to the alkaline hydrolysis of ethyl acetate and to the reaction of acetylacetone with hydroxylamine hydrochloride. For simple systems, data obtained during the first 5 to 10 min. of a reaction are capable of giving results accurate to 0·3%. G. P. COOK

2647. **Analysis of the acidic function.** E. A. M. F. Dahmen (Koninklijke/Shell-Laboratorium, Amsterdam). *Chim. Anal.*, 1958, **40** (10), 378–384.—For the titration of weak acids, the use of non-aq. solvents is recommended because of their greater "region of acidity." On comparing the half-neutralisation potentials of various acids in a selection of solvents, a comparison justified by the small influence of concn. on these values, a levelling effect is found when the half-neutralisation potential is outside the region of acidity of the solvent. Thus for the determination of the total acidity of an organic sample, a basic solvent should be chosen so that its region of acidity lies above the half-neutralisation potentials of the acids. For the simultaneous determination of the individual acids present, a less basic or even an inert solvent is used so that the half-neutralisation potentials lie within as wide a range of acidity as possible. Examples of the application of these principles are given. J. H. WATON

2648. **Simultaneous volumetric determination of maleic acid and maleic anhydride.** H. Huhn and E. Jenckel (Inst. f. theor. Hüttenkunde und phys. Chem., Tech. Hochschule, Aachen, Germany). *Z. anal. Chem.*, 1958, **163** (6), 427–429.—The method is based on the titration of the total acidity with 0·1 *N* NaOH (formation of the sodium salt of maleic acid) and with 0·1 *N* Na methoxide (formation of the sodium salt of the methyl ester). The difference between the determinations is proportional to the anhydride concentration. B. B. BAUMINGER

2649. **Chromatographic separation of erucic acid from saturated and unsaturated higher fatty acids.** A. Z. Budzyński and Z. J. Zubrzycki (Inst. of Nucl. Res., Warsaw). *Roczn. Chem.*, 1958, **32** (6), 1425–1426.—Erucic acid is separated from the mixture of higher fatty acids by reversed phase chromatography. A mixture of synthetic saturated hydrocarbons ("Mepasyn") is used as the stationary phase and 96% acetic acid as the mobile phase. The stearic acid spot appears nearest to that of erucic acid, the R_F values being, respectively, 0·29 and 0·22. H. DMOWSKA

2650. **Quantitative separation of nitrogenous organic bases using ammonium reineckate.** Lee Kum-Tatt (Dept. of Chem., Outram Road, Singapore 3). *Nature*, 1958, **182**, 655–656.—Reaction between bases and ammonium reineckate depends on the basicity of the compounds and the pH of reaction. An expression is given relating the dissociation const. pK_b of a base with pH; by determining pK_b, the pH required for complex formation can be calculated. Urea, a very weak base, gives a reineckate in strong acid soln. Bases with pK_b values sufficiently far apart can be separated by pH adjustment of the reineckate soln.; figures for recoveries from mixtures of bases are given. Other uses of the reagent are mentioned. P. D. PARR-RICHARD

2651. **Determination of nitroguanidine by reduction with buffered titanous chloride.** M. Roth and R. F. Wegman (Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2036–2038.—Nitroguanidine is quant. reduced with $TiCl_3$ in buffered soln. (pH 11·5 ± 0·5) with a gain of 6 electrons per mole. The sample is dissolved in H_2O and a portion is added to a soln. of buffer and $TiCl_3$, the excess of which is titrated with standard $(NH_4)_2SO_4.Fe_2(SO_4)_3$ soln., with NH_4SCN as indicator. The standard deviation was ≃ ± 0·04%, calculated from 10 determinations on a propellent. Good agreement was attained with the results obtained by other methods. G. P. COOK

2652. **Volumetric determination of carbon disulphide.** J. Romováček (Katedra Plynárenství a Koksárenství, Vys. Škola Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (10), 1912–1915.—Dialkyldithiocarbamic acid, formed by the reaction of CS_2 with secondary amines in a mixture of pyridine, *iso*propyl alcohol and H_2O, can be determined by titration with alkali, with thymolphthalein as indicator, or potentiometrically. Morpholine and diethanolamine are the most suitable amines. The method is useful for a rapid determination of CS_2. *Procedure*—To the solvent (pyridine - H_2O - *iso*propyl alcohol) (4:2:4) (75 ml) and 0·5 *N* morpholine or diethanolamine in pyridine (25 ml) add the sample containing 0·5 to 17 milli-equiv. of CS_2, 5 drops of 1% thymolphthalein soln. in pyridine and 0·5 *N* NaOH dropwise till the soln. is blue then 2 to 5 ml in excess. Titrate with 0·5 *N* HCl till the blue colour is discharged. The average error is ± 0·10%. The method has been tested by analysing soln. of CS_2, and determining CS_2 in the presence of H_2S, mercaptans and HCN. The procedure requires ≯ 10 min. J. ZÝKA

2653. **Infra-red spectra of xanthates and related compounds.** F. G. Pearson and R. B. Stasiak (American Viscose Corp., Marcus Hook, Pa., U.S.A.). *Appl. Spectroscopy*, 1958, **12** (4), 116–120.—Infra-red spectra of liquid paraffin mulls of several xanthates, oxyxanthates and dixanthates are shown. Constancy of frequencies within each group and correlation with molecular structure are discussed. P. T. BEALE

2654. **Titration of sulphoxides in acetic anhydride.** D. C. Wimer (Abbott Lab., N. Chicago, Ill.). *Anal. Chem.*, 1958, **30** (12), 2060–2061.—Sharp end-point inflections in acetic anhydride were obtained with several aliphatic, aromatic and heterocyclic sulphoxides, but mixtures of sulphoxides could not be resolved. A 0·001-mole sample is dissolved in

75 ml of acetic anhydride and titrated potentiometrically with standard 0·1 *N* $HClO_4$ in dioxan (*cf. Anal. Chem.*, 1958, **30**, 77, 997). Sulphides and sulphones do not interfere.

P. D. PARR-RICHARD

2655. **The infra-red spectra of methoxy-, methylmethoxy- and methoxy-end-blocked dimethylpolysiloxanes.** Toshio Tanaka (Appl. Chem. Dept., Engng Faculty, Osaka Univ., Miyakojima-ku). *Bull. Chem. Soc. Japan*, 1958, **31** (6), 762–766 (in English).—The i.r. spectra of the lower members of methoxy-, methylmethoxy- and methoxy-end-blocked dimethylpolysiloxanes are compared with those of dimethyl ether, dimethylpolysiloxanes, etc. The characteristic absorption band of the $Si{\cdot}OCH_3$ group appears near 1190 cm^{-1}. Except in the case of the first members of these alkoxysiloxanes, a spectral sequence corresponding to the structural unit sequence of SiO_4, SiO_3C and SiO_2C_2 is observed in the region of 1000 to 1100 cm^{-1}.

I. JONES

2656. **Direct mass-spectrometric determination of the content of deuterium in deuterobenzene.** G. A. Semenov and M. Ya. Turkina (State Inst. of Appl. Chem). *Zavod. Lab.*, 1958, **24** (9), 1084–1086.—Direct determination from measurements of the mol. peaks obtained with a MS-4 mass spectrometer at an ionisation energy of 14 eV is described.

G. S. SMITH

2657. **Coulometric determination of styrene and methyl oleate in the presence of each other.** F. Čůta and V. Klozar (Inst. Anal. Chem., High-School of Chem. Technol., Prague). *Chem. Listy*, 1958, **52** (10), 1899–1902.—The different rates of addition of bromine to methyl oleate (**I**) and styrene (**II**) in acetic acid medium have been used for the coulometric determination of **I** in admixture with **II**. The velocity of the reaction with **I** is 13 times as great as that with **II**. The rate of addition of chlorine is very high and can be used for the determination of the total of **I** and **II**. Amperometric indication of the end-point has been used. The coulometric titration of **II** has been carried out in 13 to 14 *N* acetic acid by generating chlorine from 0·5 to 1·5 *N* HCl. The average error is ± 0·15% for about 1 mg of **II**. The titration of **II** with bromine generated from 0·5 to 1 *N* HBr is quant. if the titration is carried out in 9 to 12 *N* acetic acid. **I** can be determined in 10·5 to 14·0 *N* acetic acid by generating bromine from 0·5 to 1 *N* HBr. The total of **I** and **II** can be determined in 15 to 16 *N* acetic acid containing 1·2 *N* HCl. The average error is ± 0·24%. **I** in the presence of **II** can be determined in 15 to 16 *N* acetic acid containing 0·5 *N* HBr; only one end-point, corresponding to the amount of **I**, is observed. If the ratio of **I** to **II** is > 1:9, a positive error occurs. The coulometric titration has been carried out in a vol. of 20 ml, at 10 mA. The generating cathode is placed in a vessel filled with 38% HBr or 20% HCl and is separated from the sample soln. by a porous glass partition.

J. ZÝKA

2658. **Gas-liquid chromatography of stereoisomeric methylcyclohexanols.** R. Komers, K. Kochloefl and V. Bazant (Inst. Chem., Czech. Acad. Sci., Prague). *Chem. & Ind.*, 1958, (43), 1405–1406.—Good separation of mixtures of *cis*- and *trans*-2-methyl-, 3-methyl-, or 4-methyl-*cyclo*hexanols can be achieved by gas-liquid partition chromatography by using stationary phases capable of hydrogen bond formation, *e.g.*, glycerol (17%) or erythritol (25%) on Celite 545; nitrogen was used as carrier gas. Ketones do not interfere since their retention vol. are much smaller than those of the corresponding alcohols. The method is capable of further extension to other cyclic alcohols.

G. P. COOK

2659. **Chromatographic determination of phenol in technical o-cresol.** V. Lakota (Východočeské Chem. Závody, Synthesia, Pardubice-Semtín, Czechoslovakia). *Chem. Listy*, 1958, **52** (10), 1922–1925.—The chromatography is carried out on a column of kieselguhr treated with triethoxyethylsilane, with $CHCl_3$ - H_2O as eluent. Phenol is eluted first, followed by cresol. 2:6-Dibromo-*p*-benzoquinonechlorimine is used for the detection. *Procedure*—Kieselguhr (200 g) is mixed with triethoxyethylsilane (20 ml) in water-free CCl_4 (480 ml) and the suspension is dried for 5 hr. at 160°. The product (200 g) is mixed with $CHCl_3$ (5 × 150 ml) saturated with H_2O, and packed in a chromatographic column (55 cm × 2 cm) to a depth of 40 cm. This method has been tested by analysing a mixture containing phenol (10 μg), *m*-cresol (10 μg) and *o*-cresol (20 μg) in 1 ml, which is washed on to the column with H_2O (3 × 1 ml). The column is eluted with H_2O saturated with $CHCl_3$ at 2·5 ml per min. A 10-ml aliquot of the eluate is diluted with borate buffer soln. (pH 9·4) (20 ml) and an ethanolic soln. of 2:6-dibromo-*p*-benzoquinonechlorimine (1%) (0·1 ml), then made up to 50 ml, and the extinction measured at 620 mμ. The procedure is suitable for the determination of phenol in technical products.

J. ZÝKA

2660. **Gas-liquid partition chromatography. Determination of 2:6-di-*tert.*-butyl-*p*-cresol on antioxidant-treated paperboard.** E. C. Jennings, jun., T. D. Curran and D. G. Edwards (Fibreboard Paper Products Corp., Antioch, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1946–1948.—The paperboard is extracted with *cyclo*hexane - *iso*propyl alcohol (9:1), followed by concentration of the extract to 8 to 10 ml. An aliquot of this soln. is chromatographed on propylene glycol on firebrick, with He as carrier gas. The quantity of 2:6-di-*tert.*-butyl-*p*-cresol is directly proportional to the area under the recorded peak. Recoveries of 100 ± 10% over the concn. range of 14·4 to 144 mg per sq. ft. or 0·05 to 0·5% by wt. of the paperboard were obtained.

G. P. COOK

2661. **Spectrophotometric determination of 4-*tert.*-butylcatechol and o-aminophenol in 2-methyl-5-vinylpyridine.** K. H. Nelson and M. D. Grimes (Phillips Petroleum Co., Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1928–1930.—The sample is dissolved in *N* HCl and the 4-*tert.*-butylcatechol (**I**) is extracted into diethyl ether; **I** is then extracted with *N* NaOH and, after air oxidation to the coloured quinonoid form, the extinction is measured at 485 mμ. The *o*-aminophenol (**II**) is determined by dissolving the sample in *n*-heptane and extracting with 0·1 *N* HCl. The acid phase is buffered with ammonium acetate - acetic acid and **II** is oxidised with H_2O_2; the extinction is measured at 435 mμ. The relative errors are 4·5 and 1·1% and the precision is ± 1·4 and 1·3% for the **I** and **II** determinations, respectively.

G. P. COOK

2662. **Phthalocyanines as oxidation - reduction indicators. III. Use of copper phthalocyanine-tetrasulphonic acid. Titration of quinol and metol with ceric sulphate solution.** T. P. Sastri and G. Gopala Rao (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1958, **163** (4), 263–266 (in English).—Copper phthalocyanine-tetrasulphonic acid (**I**) is a satisfactory internal indicator in the titration of quinol and metol with $Ce(SO_4)_2$ soln. The end-point is indicated by a sharp change in colour from blue - green to light yellow. *Procedure*—An aliquot of the metal soln. is treated with 10 ml of 4 *N* H_2SO_4 and the mixture is diluted to 100 ml with H_2O. Indicator soln. (0·1%, 2 drops) is added before titrating with standard $Ce(SO_4)_2$ soln. No indicator correction is necessary with 0·05 *N* or 0·1 *N* $Ce(SO_4)_2$. With 0·1 *N* soln. an indicator correction of 0·02 ml should be applied. These values agree within ± 0·1% with those obtained by the potentiometric end-point method. B. B. BAUMINGER

2663. **Analysis of mixtures of terephthaloyl and *iso*phthaloyl chlorides.** E. J. Breda (E. I. du Pont de Nemours & Co., Gibbstown, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2020–2022.—Terephthaloyl and *iso*phthaloyl chlorides are determined in mixtures containing both acid chlorides and corresponding free acids. The acid chlorides are dissolved in *iso*octane and the insol. free acids are filtered off; the extinction of the soln. is measured at 227 and 263 mμ. The concn. of the acid chlorides are calculated from simultaneous equations. The average error is ± 0·6% and ± 1·3% absolute for the terephthaloyl and the *iso*phthaloyl chloride determinations, respectively, in the 0 to 100% range. The most suitable working range is 5 to 95% of acid chloride. G. P. COOK

2664. **Paper-chromatographic determination of methyl *p*-toluate in the presence of dimethyl terephthalate.** J. Franc (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (10), 2004–2005.—Methyl *p*-toluate (**I**) and dimethyl terephthalate (**II**) can be converted by means of hydroxylamine hydrochloride (**III**) to the corresponding hydroxamic acids, which can be separated chromatographically and detected with $FeCl_3$ soln. The amount of **III** used for the reaction can be reduced by dissolving the sample in ethanol in which **I** is readily soluble, whilst the solubility of **II** can be neglected. *Procedure*—Heat the sample of technical **II** (5·0 g) with ethanol (96%) (50 ml) until dissolution is complete, then cool. Filter off the crystals of **II** and wash with ethanol (3 × 10 ml). Evaporate the filtrate to 20 ml and repeat the filtration and the washing with ethanol (3 × 5 ml). Evaporate to 10 ml, filter again and add to the filtrate a freshly prepared soln. of **III** (mix one part of 5% ethanolic **III** soln. with two parts of 5% ethanolic KOH soln. and filter off the KCl) (40 ml). Heat for exactly 10 min., cool, filter into a 25-ml cylinder and dilute to vol. Separate 0·025 ml of this soln. chromatographically with the use of Whatman paper No. 4, ascending technique, and a mixture of *n*-butanol - ethanol - H_2O (2:2:1) as solvent. Dry the chromatogram, then moisten it with $FeCl_3$ soln. [2% in ethanol - butanol (1:4)]. Compare the intensity of the blue - violet spots (R_F 0·78) with that of spots on a calibration scale prepared with the use of pure **I** as standard.

J. ZÝKA

2665. **The automatic titration of primary aromatic amines with nitrous acid.** L. T. Butt and H. E. Stagg (Anal. Dept., I.C.I. Ltd., Dyestuffs Div., Manchester). *Anal. Chim. Acta*, 1958, **19** (3), 208–215 (in English).—The "dead stop" and potentiometric titrations with HNO_2 have been studied for sulphanilamide, *p*-nitroaniline, *o*-dianisidine, *o*-anisidine and benzidine. The conditions for the dead-stop end-point (the addition of 5 g of NaBr and 300 mV applied e.m.f.) give excellent results for both manual and automatic titration except with *o*-dianisidine, which gives an abnormal curve unsuitable for automatic titration. A high initial current, which would invalidate automatic titration, was caused by the presence of 1% of Cu^{II} or of Fe^{III}. Potentiometric titration gave good results for all the amines examined in the presence and absence of Cu^{II} and Fe^{III}. T. R. ANDREW

2666. **Spot tests for ascertaining the purity of NN-dialkylanilines.** F. Feigl and E. Jungreis (Lab. da Prod. Mineral, Min. da Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1958, **47** (3), 64.—Monoalkylaniline (**I**) and aniline (**II**) can be detected in dialkylaniline (**III**) by dissolving 1 drop of sample in ether (1 to 2 ml), placing 1 drop of soln. in a micro test-tube containing a few mg of hexamine, evaporating the ether, closing the mouth of the tube with filter-paper moistened with Nessler's soln., and heating in a boiling-water bath. In the presence of **I** or **II**, a yellow to brown stain forms on the paper in 1 to 2 min., the shade depending on the amount of impurity; 10 μg of **I** or 5 μg of **II** can be detected in 1 drop of **III**. To distinguish **II**, a drop of the ether soln. is placed on a paper impregnated with ethereal *p*-dimethylaminobenzaldehyde. A yellow stain indicates the presence of **II**.

R. E. ESSERY

2667. **Chromatography of some aromatic amines with Japanese acid clay.** Daisei Yamamoto (Fac. of Sci., Kumamoto Univ.). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (9), 1030–1032.—When an aromatic amine in water or in an aromatic hydrocarbon is dropped on a thin layer of colourless montmorillonite clay, a characteristic colour develops annularly (*e.g.*, *o*- and *p*-phenylenediamine, red and dark blue, respectively; benzidine, blue; *o*- and *p*-anisidine, grey - violet and blue, respectively; diphenylamine, green). This reaction can be applied to the chromatographic detection of various binary and ternary mixtures. K. SAITO

2668. **New reagent for titrations in non-aqueous medium. III. Determination of derivatives of aniline and pyridine, and esters of *p*-aminobenzoic acid with the chloroaluminium *iso*propoxide hydrochloride complex.** G. Tokár and I. Simonyi (United Pharm. and Food Factories, Budapest). *Magyar Kém. Foly.*, 1958, **64** (10), 379–382.—The chloroaluminium *iso*propoxide hydrochloride complex, described previously (*Ibid.*, 1958, **64**, 94 and 151), is used for the determination of weak bases with dissociation constant $K_b > 10^{-10}$. The titration is carried out in $CHCl_3$, benzene, chlorobenzene or xylene. Dimethyl yellow or ethyl orange indicator is employed. Aniline, *p*-anisidine or *p*-phenetidine can be determined with $\geqslant 1\%$ error. *p*-Phenetidine can be titrated with $< 15\%$ of chloroaniline present, as the latter does not react with the titrant. When procaine or amethocaine is titrated, only the basic nitrogen on the side-chain reacts. G. SZABO

2669. **Determination of dioctyldiphenylamine in hydraulic fluids.** S. W. Nicksic and S. H. Judd (Calif. Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2002–2004.—The method is based on the reaction of *pp'*-dioctyldiphenylamine with furfuraldehyde in the presence of conc. H_2SO_4. The resulting yellow colour is measured at 385 mμ. The reaction is a general one and certain other amines will interfere. The average deviation is ± 2% in the 1 to 2% range and ± 5% in the 0·2 to 1% range of added *pp'*-dioctyldiphenylamine. G. P. Cook

2670. **Application of the titanometric method to the analysis of indophenols.** V. Paul, S. Hoffman and B. Jacob. *Rev. Chim., Bucharest*, 1958, **9** (10), 576–577.—Two methods are proposed, depending on the nature of the indophenol. (*i*)—Procedure for indophenols derived from diphenylamine (quinoneimine form). Approx. 0·1 g of the indophenol paste is dissolved in 50 ml of H_2SO_4 at 0°, the acid being added dropwise. This is then diluted to 200 ml with H_2SO_4 (73%), keeping the temp. between 0° and 5°. A current of CO_2 is bubbled through 50 ml of the liquid for 10 min., then 0·1 *N* $TiCl_3$ is rapidly added in excess until the soln. is completely decolorised and then passes back to pale violet. The excess of $TiCl_3$ is back-titrated with $K_2Cr_2O_7$ (0·2 *N*) until a permanent blue colour with diphenylamine is obtained. (*ii*)—Procedure for derivatives obtained by condensation of 1-naphthylamine-6- or -7-sulphonic acid or N-phenylnaphthylaminesulphonic acid with *p*-aminophenol (leuco derivatives). The derivative is first oxidised to the quinoneimine form with hypochlorite, and then titrated with 0·1 *N* $TiCl_3$. About 6 g of the leucoindophenol is suspended in ≃ 200 ml of cold H_2O (0° to 2°) and NaOH is added to a pH of 11. The soln. is diluted to one litre with boiled H_2O at the same temp., 50 ml is taken and treated with 0·5 to 4 ml of NaOCl soln. (≃ 1% total Cl); 1 min. later, 20 ml of Na citrate soln. (20%) and 2 g of Na_2CO_3 (solid) are added. The soln. is titrated with 0·1 *N* $TiCl_3$ to a yellow-brown colour, and excess of $TiCl_3$ is then added. After acidification with 20 ml of HCl, 5 ml of a soln. of NH_4SCN (10%) is added, and the soln. is titrated with 0·1 *N* $(NH_4)_2SO_4.Fe_2(SO_4)_3$ to a persistent brown-violet colour. H. Sher

2671. **Quantitative colorimetric determination of benzimidazolone and some derivatives.** C. C. Porter (Merck, Sharp & Dohme Res. Lab., West Point, Va., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2063–2064.—These compounds were easily extracted from blood plasma with a solvent such as ethyl acetate - $CHCl_3$ (2:1). Residues remaining after evaporation of the extract were assayed by two methods. The first depended on the fluorescence of the compounds dissolved in 0·1 *N* HCl. The other was based on measurement of the red colour produced with chromic acid in the presence of a specified concn. of ethanol. G. P. Cook

2672. **Determination of toluenesulphonic acids in presence of an excess of sulphuric acid.** S. Pinchas and P. Avinur (Weizmann Inst. Sci., Rehovoth, Israel). *Anal. Chem.*, 1958, **30** (12), 2022–2023.—The total concn. of the three isomers of toluenesulphonic acid are spectrophotometrically determined by measurement at 222 mμ. A mean absorptivity coeff. of 60 (for a soln. containing 1 g of monohydrate per litre) is used. The deviation of the method for known concn. of isomers was ± 3% in the concn. range 0·00257 to 0·00797 g per litre. The mean deviation was + 1·8% for 5 determinations. G. P. Cook

2673. **Identification of organic compounds. XXVI. X-ray diffraction patterns of SS-dialkyl-N-*p*-tolylsulphonylsulphilimines.** D. Šnobl, V. Kadaníková, J. Petránek and M. Večeřa (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1958, **52** (8), 1537–1545.—X-ray patterns of *p*-tolylsulphonylsulphilimine derivatives of 23 thio ethers were measured and proved reliable for the identification of these compounds. It has been found that the values of interplanar spacings intervals *d*, when determined with the use of the common technique for organic compounds having a big elementary cell and low symmetry, can be distorted owing to superposition, thus showing considerable deviations from tabulated values. J. Zýka

2674. **Infra-red spectra of fluorocycloolefins.** J. Burdon and D. H. Whiffen (Birmingham Univ., England). *Spectrochim. Acta*, 1958, **12** (2–3), 139–142.—The –C:C– stretching frequencies of several different types of highly fluorinated six-membered-ring olefins have been measured. In the vapour phase those compounds with two fluorine atoms on the double bond absorb near 1749 cm^{-1} and those with one hydrogen and one fluorine atom absorb near 1719 cm^{-1}, while those with two hydrogen atoms on the double bond (only two such compounds were examined) showed no marked absorption in the region and could be mistaken for saturated compounds. The frequencies of related *cyclo*hexadienes are also discussed. E. G. Cummins

2675. **Rapid method for the determination of acenaphthene.** J. Jurkiewicz, J. Janczur, A. Orzechowska and J. Rząsa (Zakład Przerobu Węglopochodnych Inst. Chem. Przeróbki Węgla, Zabrze, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 147–157.—In the method described, use is made of the relation between the melting-point *t*, or the freezing-point *t'*, of a sample and the amount of acenaphthene contained in the sample. The following relationships have been derived—(*a*) $P = 1{\cdot}4 \times t - 33$, and (*b*) $P = 1{\cdot}5 \times t' - 42{\cdot}5$, where *P* is the percentage of acenaphthene in the sample. The method is suitable for samples containing 50 to 100% of acenaphthene, and results are accurate to within ± 1%. The procedure takes only 20 min., as against 16 hr. for the picric acid method, and results by the two methods show good agreement. S. Wasilewski

2676. **Thermochromic test for polycyclic *p*-quinones.** E. Sawicki, T. W. Stanley and T. R. Hauser (U.S. Dept. Health, Educ. and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1958, **30** (12), 2005–2006.—Many compounds that contain the quinonoid structure show a reversible thermochromic reaction. The only compounds that do not contain this structure, but give a positive test, are fluorenone and 2:3-benzofluorenone. All the tested unsubstituted polynuclear *p*-quinones and some derivatives of anthraquinone gave a colour reaction. Data for ≃ 30 compounds are listed. G. P. Cook

2677. **Low-temperature chromatography as a means for separating terpene hydrocarbons.** R. L. Clements (Dept. of Plant Biochem., Univ. of Calif., Riverside, U.S.A.). *Science*, 1958, **128**, 899–900.—

Preliminary separation of terpenes is necessary before gas chromatography, and may be carried out by column chromatography at the temp. of solid CO_2 (— 78·5°) in a special column designed for immersion in a vacuum flask. Silicic acid is prepared by washing by the method of Bulen *et al.* (*Anal. Chem.*, 1952, **24**, 187) and drying at 150° for 48 hr. or longer. The technique of column chromatography followed by gas chromatography of the fractions is described. H. F. W. KIRKPATRICK

2678. **Spectrophotometric determination of complexing agent in a polynitroaromatic molecular compound.** L. H. Klemm, J. W. Sprague, H. Ziffer and B. I. Macgowan (Univ. of Oregon, Eugene, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 369–371.—The procedure involves comparison of the extinctions of solutions of the mol. compound of naphthalene and its derivatives) and its complexing agent over a range of wavelengths at which the absorption by the complexed substance is negligible. H. N. S.

2679. **Ultra-violet absorption spectra of derivatives of symmetric triazine. II. Oxo-triazines and their acyclic analogues.** R. C. Hirt and R. G. Schmitt (American Cyanamid Co., Stamford, Conn.). *Spectrochim. Acta*, 1958, **12** (2–3), 127–138.—The u.v. absorption spectra of the oxygen-containing symmetrical triazines, their ions, and acyclic analogues are correlated with their molecular structures in terms of conjugated double bonds between C and N atoms of the heterocyclic ring and exocyclic N and O atoms. The probable structure of 2:4:6-triamino-*sym.*-triazine is deduced from these correlations. Spectrophotometrically determined ionisation constants (*cf.* King and Hirt, *Appl. Spectroscopy*, 1953, **7**, 164) are reported.
E. G. CUMMINS

2680. **Ultra-violet absorption vapour spectra of pyrazine and chloropyrazine.** R. C. Hirt (American Cyanamid Co., Stamford, Conn.). *Spectrochim. Acta*, 1958, **12** (2–3), 114–126.—The u.v. absorption frequency of pyrazine vapour and of chloropyrazine vapour are analysed in terms of ground-state and excited-state vibrational frequencies, and combinations thereof. Analyses of the "sharp" band systems of both pyrazine and chloropyrazine (attributed to "n-to-π^*" transitions involving the non-bonding electrons of the heterocyclic nitrogen atoms) are presented. Only the "diffuse" system, attributed to a "π-to-π^*" "benzenoid" transition of pyrazine vapour showed enough detail to permit any attempt at assignments. Extremely weak bands have been observed at lower energies in solution or liquid phases which show a substantial "blue shift" between pyrazine and chloropyrazine. These are attributed to an "n-to-π^*" singlet - triplet transition. Infra-red and Raman data for chloropyrazine are presented for comparison purposes.
E. G. CUMMINS

2681. **Separation of saturated hydrocarbons from petroleum residues.** R. D. Schwartz and D. T. Brasseaux (Shell Development Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1999–2002.—A chromatographic adsorption procedure, which does not entail preliminary removal of asphaltenes and resins, is described for the isolation of saturated hydrocarbons from crude oil residues. *cyclo*Hexane is used as the solvent and the column is packed with Davison grade-70 silica gel above Davison grade-912 silica gel. The grade-70 packing has larger pores, which adsorb asphaltic and resinous matter; the grade 912, with smaller pores, adsorbs the simpler aromatics. Ultra-violet analysis of suitable saturates indicates that the aromatic content is $< 5\%$. The results show that pore size is a very important factor in the adsorption separation of heavy petroleum fractions. G. P. COOK

2682. **Determination of adamantane in petroleum, based on the formation of adducts with thiourea.** S. Landa and S. Hála (Inst. Synth. Materials, High School Chem. Technol., Prague). *Chem. Průmysl*, 1958, **8** (8), 395–397.—Adamantane (tri*cyclo*-[3:3:1:$1^{3,7}$]-decane) (**I**) forms a crystalline adduct with thiourea, which can be isolated and determined gravimetrically. *Procedure*—Steam-distil 2 kg of petroleum until 8 to 10% has been distilled. Filter the distillate through 1 to 2 g of activated silica gel and to the filtrate add powdered thiourea and methanol (17 g of thiourea and 22 ml of methanol for 170 g of distillate) and mix for 2 hr. at 18°. Filter off the formed adduct and wash with a few ml of pentane. Dry for 30 min. with a current of air and transfer the ppt. to a vessel containing 500 ml of H_2O. Heat under reflux to decompose the adduct, then steam-distil. Collect 100 ml of distillate, separate the organic phase (10 to 12 ml) and cool to — 50° to — 70°. Crystals of **I** are formed, which can be filtered off and purified by recrystallisation from methanol, weighed and identified by m.p. and elementary analysis. The results are lower than theoretical values, because of the volatility and solubility of **I**, but the method can be used for routine analysis. An average of $\lessapprox 0{\cdot}02$ to $0{\cdot}03\%$ of **I** was found in various types of Czechoslovakian petroleum and other crude oils of naphthenic type. J. ZÝKA

2683. **Estimation of types of nitrogen compounds in shale-oil gas oil.** G. U. Dinneen, G. L. Cook and H. B. Jensen (Bureau of Mines, Laramie, Wyo., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2026–2030.—A systematic procedure is described. First, the nitrogen compounds were concentrated by adsorption on Florisil and were then separated into fractions by mol. distillation and thermal diffusion. The fractions were analysed by mass-spectral, physical and chemical methods. The types of compound present were deduced by interpreting the similarities and differences shown in the spectra of a series of fractions. Pyridines, dihydropyridines, indoles and quinolines comprised over half the nitrogen compounds in the gas oil. Much of the remainder consisted of compounds having one or more saturated rings condensed with these.
G. P. COOK

2684. **X-ray determination of sulphur in oils. Comparison of X-ray emission and absorption methods.** W. R. Doughman, A. P. Sullivan and R. C. Hirt (Res. Div., Amer. Cyanamid Co., Stamford, Conn., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1924–1925.—Both the X-ray spectrographic method and the ^{55}Fe *K*-capture X-ray absorption procedure have the same accuracy; the former method is less susceptible to interference but is more costly than the latter. K. A. PROCTOR

2685. **Determination of phosphorus in solid fuels.** W. Radmacher and W. Schmitz (Brennstoffchem. Inst. der Ruhrkohlen-Beratung G.m.b.H., Essen, Germany). *BrennstChem.*, 1958, **39** (17–18), 274–279.—In view of the possible loss of P during the oxidation of the sample, a series of coals of phosphorus contents 0·005 to 0·05% have been tested

by four methods, namely combustion in a muffle-furnace followed by HF - H_2SO_4 treatment of the ash; combustion with Eschka mixture; oxidation by H_2SO_4 assisted by HNO_3 or by Se. No significant differences were found. The oxidation of coke can be safely accelerated by heating the ground sample in a platinum crucible and directing down on it, through a quartz tube, a stream of O, regulated so as to keep the temp. at $\nearrow$ 1000°.

A. R. PEARSON

2686. **Determination of soluble chloride in coal-carbonisation products by water - *iso*butyl methyl ketone extraction.** L. Ginsburg and L. C. Pasztor (Jones & Laughlin Steel Corp., Pittsburgh, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2039–2040.—The water-soluble chlorides are extracted from an *iso*butyl methyl ketone soln. of the sample with H_2O and are determined by the Mohr titration procedure. Copper nitrate is added to precipitate interfering substances such as sulphide. Procedures are given for coal-tar acid, tar-acid oil, raw tar and crude Na phenoxide samples. Recoveries are $\simeq$ 100%.

G. P. COOK

2687. **Automatic determination of sulphur trioxide in flue gases.** P. H. Crumley, H. Howe and D. S. Wilson (Fuel Res. Sta., D.S.I.R., London). *J. Inst. Fuel*, 1958, **31**, 378–382.—The method of determining SO_3 by absorption in *iso*propyl alcohol soln., pptn. as $BaSO_4$ and photo-electric measurement of the resulting suspension (Corbett, *J. Inst. Fuel*, 1951, **24**, 247) has been made automatic by a 16-stage process. Details of construction are given. The apparatus was used to determine concn. of 10 to 50 p.p.m. with an accuracy of $\pm$ 5% in the middle range. This scatter was smaller than that given by the manual method. There is a lag of 20 min. before complete response to a change in SO_3 concn. is obtained.

P. M. SORGO

2688. **Application of ion exchangers in detergent analysis.** P. Voogt (Unilever Res. Lab., Vlaardingen, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1958, **77** (9–10), 889–901.—Detergent mixtures containing sodium salts of alkylsulphuric or sulphonic acids with fatty acids and non-ionic material can be separated into three fractions (strong acid, weak acid and non-ionic material) by passage in ethanolic soln. over three exchangers, namely Dowex 50-X8 (H), Dowex 1-X2 (acetate) (**I**) and Dowex 2-X8 (OH) (**II**). Fatty acids (eluted from **II**) and sulphonic acids (eluted from **I**) may be determined potentiometrically, and both the content and mol. wt. of the acids can be calculated. The content of non-ionic material (present in the eluate) may be obtained gravimetrically. The method was tested with Na dodecylsulphonate and Na dodecoate.

J. M. HUBBARD

2689. **Colorimetric micro-determination of nitrogen in cellulose nitrates by the phenoldisulphonic acid method.** J. L. Gardon and B. Leopold (Ind. Cellulose Res., Ltd., Hawkesbury, Ont., Canada). *Anal. Chem.*, 1958, **30** (12), 2057–2060.—The method is based on the reaction of cellulose nitrate with phenoldisulphonic acid to produce, after neutralisation, an intense yellow colour which is measured at 400 mμ. The intensity is proportional to the N content at constant pH and is higher for cellulose nitrate than for inorg. nitrate if the pH is $>$ 6. Above pH 8 the colour intensity is affected by atmospheric O. The accuracy is within $\pm$ 2% for 0·2 to 0·8-mg samples in the pH range 7·1 to 7·5. The precision of a single determination (95% confidence limits) is $\pm$ 2·3%.

G. P. COOK

2690. **Rapid determination of zinc in viscose spinning liquor.** Mikihiko Saito, Seiko Nagamura and Keihei Ueno (Dojindo & Co., Ltd., Kunamoto, Japan). *Chemist Analyst*, 1958, **47** (3), 67–68.—The sample (5 to 15 mg of Zn) is diluted to between 50 and 100 ml, neutralised with NaOH to phenolphthalein, treated with 5 ml of acetate buffer (pH 5·2) and titrated with 0·1 *M* EDTA (disodium salt), in the cold with xylenol orange, or near boiling-point with copper - PAN, as indicator. These indicators have about equal sensitivity, but xylenol orange is more tolerant with respect to interference. Alkaline-earth metals are not co-titrated, but bivalent cations are, although the amounts (10 to 50 p.p.m.) usually present in viscose liquors do not affect the limit of error (0·3%) permitted in routine control. Aluminium and Fe are co-titrated when copper - PAN is used, but Al does not interfere with xylenol orange if the titration is conducted rapidly, nor does Fe in amounts $<$ 500 p.p.m. Ferric iron is not masked by reduction with hydrazine or ascorbic acid; Al can be masked with tiron (in the absence of Fe) or tartrate, but a large excess of tartrate masks some of the Zn. The use of NH_4F reduces the sensitivity of the indicators. Copper can be masked with thiourea.

R. E. ESSERY

2691. **Determination of *cyclo*hexanone oxime by means of *p*-nitrophenylhydrazine and 2:4-dinitrophenylhydrazine.** S. Goszczyński (Katedra Technol. Chem. Organ., Politech. Śląskiej, Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 107–115.—*Detection*—To an aq. soln. of the sample (at pH 3 to 7) add a 5% aq. soln. of *p*-nitrophenylhydrazine hydrochloride (**I**). A yellow colloidal suspension is formed immediately if the concn. of the oxime is $>$ 0·001 g per ml, or after a few minutes if the concn. is 0·2 to 1 mg per ml. Caprolactam does not affect the reaction. Alternatively, add a satd. soln. of 2:4-dinitrophenylhydrazine (**II**) in 2 *N* HCl to an aq. soln. of the sample. A yellow turbidity is formed in the presence of $\lessdot$ 0·02 mg of the oxime per ml. A maximum reaction time of 7 min. should be allowed. *Quantitative determination*—Add about a 50% excess of **I** soln., with stirring, to an aq. soln. of the sample containing $\lessdot$ 0·005 g of oxime per ml. Pptn. is complete in 5 hr., or, in the presence of a large amount of lactam, in 10 hr. Collect the ppt. in a sintered glass crucible, No. 3, and wash it free from Cl^- with water. Dry the ppt. at 105°. The error is $<$ 1%. Optimum conditions are a 50% excess of the reagent, a concn. of oxime of 10 mg per ml and an absence of free HCl. Alternatively, to an aq. or ethanolic soln. of the sample containing $\lessdot$ 0·05 mg of oxime per ml add **II** (75 to 100 ml per 0·1 g of oxime). Stir until the ppt. coagulates, then set aside for 6 to 12 hr. Collect the ppt. in a No. 3 sintered glass crucible, wash with water until free from Cl^-, and dry at 110°. The error is $\nearrow$ 1·2%. Caprolactam does not interfere. The methods described are unsuitable in the presence of *cyclo*hexanone.

S. WASILEWSKI

2692. **Quantitative determination of *cyclo*hexanone oxime by determining the products of its hydrolysis.** S. Goszczyński (Katedra Technol. Chem. Organ., Politech. Śląskiej, Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 117–121.—*cyclo*Hexanone and

hydroxylamine are produced when the oxime is treated with a slight excess of 10% HCl and steam-distilled. The ketone is determined in the distillate by pptn. with 2:4-dinitrophenylhydrazine and the hydroxylamine is determined in the residue after distillation by titration with permanganate. The method is suitable for the analysis of *cyclo*hexanone oxime - *cyclo*hexanone mixtures. The error is ≯ 1·5%. S. WASILEWSKI

2693. **Quantitative determination of ϵ-caprolactam.** S. Goszczyński (Katedra Technol. Chem. Organ., Politech. Śląskiej, Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 123–129.—*Procedure*—Hydrolyse the ϵ-caprolactam with 10% HCl by heating under reflux for 1·5 hr., and determine the ϵ-aminocaproic acid obtained by (*i*) volumetric determination of the carboxyl group or (*ii*) determination of the amino group by the Van Slyke method. (*i*) First determine the total acidity (HCl plus ϵ-aminocaproic acid) after hydrolysis by titrating in alcoholic medium (80% alcohol) with alcoholic NaOH, with thymolphthalein as indicator and a colour standard (0·0025 *N* $CuCl_2$ in an excess of aq. NH_3), then determine HCl by titrating with 0·1 *N* $AgNO_3$ (Mohr). The error ranges from − 1·5 to + 0·5%. (*ii*) Shake the reactants for 25 to 30 min. at 20° and determine the ϵ-caprolactam from the vol. of N evolved. The error ranges from − 0·5 to + 1·5%. S. WASILEWSKI

2694. **Analysis of mixtures of ϵ-caprolactam, *cyclo*hexanone oxime and *cyclo*hexanone.** S. Goszczyński (Katedra Technol. Chem. Organ., Politech. Śląskiej, Gliwice, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 131–135.—The mixture is treated with 10% HCl and steam-distilled until the residue is free from *cyclo*hexanone. The residue is then heated under reflux, the total period of heating being 1·5 hr. The analysis is carried out as described earlier (*cf. Anal. Abstr.*, 1959, **6**, 2691, 2692, 2693), but, in the determination of ϵ-aminocaproic acid by Mohr's method, the hydroxylamine must first be decomposed with H_2O_2, and, in the determination by Van Slyke's method, the hydroxylamine must be decomposed by chromic acid (10 g of CrO_3 in 18 g of glacial acetic acid). S. WASILEWSKI

2695. **Determination of free phenol in phenol-formaldehyde resins.** R. Dijkstra and M. F. Lammers (Philips Res. Lab. N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands). *Rec. Trav. Chim. Pays-Bas*, 1958, **77** (9–10), 933–934.—The time taken for this determination may be considerably reduced by the addition of ethanediol as plasticiser to the resin during the steam-distillation. For example, 30 ml of ethanediol is added to approx. 5 g of the homogenised resin (containing about 5% of free phenol). Distillation is continued until 750 to 800 ml of distillate is obtained. Ethanediol in the distillate does not interfere with the determination. J. M. HUBBARD

2696. **Colorimetric determination of the end-point in the titration of tannin compounds with the use of the Löwenthal method.** V. Zitko (Dept. of Carbohydrates and Biochem., Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (9), 533–542.—The accuracy of the visual manganometric titration of tannin compounds has been increased by photometric indication of the end-point (IF465 filter). J. ZÝKA

2697. **Provisional methods of analysis [of leather].** Society of Leather Trades' Chemists. *J. Soc. Leath. Tr. Chem.*, 1959, **43** (4), 102–108.—Provisional methods are given for the analysis of alkaline beamhouse liquors, for the determination of pH of alkaline liquors and for the determination of S^{2-} and Cl^-. N. E.

2698. **Determination of diethyl and dibutyl phthalates in propellents.** G. Norwitz (Pitman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 216–223 (in English).—Extract 5 g of sample overnight with 125 ml of diethyl ether. Evaporate the ether extract to dryness and add 35 ml of 60% acetic acid. Heat almost to boiling, remove from the source of heat and add 6 g of zinc dust in small quantities. Heat for 5 min., cool to room temperature, add 200 ml of H_2O and decant into a separating-funnel. Wash the zinc by decantation with H_2O (2 × 50 ml). Extract with light petroleum (2 × 60 ml), and repeat the extraction on the aqueous extract. Combine the light petroleum fractions and evaporate to dryness. Saponify in the usual manner and calculate as diethyl or dibutyl phthalate. T. R. ANDREW

2699. **Colorimetric determination of stabilisers in propellents.** J. Grodzinski (Lab. Military Industries, Min. Defence, Israel). *Bull. Res. Council Israel, A*, 1957, **7** (1), 21–28.—Procedures are given for determining "ethyl centralite" (NN'-diethylcarbanilide) (**I**) and diphenylamine (**II**), each to within ≃ 2%. For **I**, the dry sample (40 mesh) is heated for 30 to 40 min. with 84% acetic acid (64% if nitrocellulose is present) and the filtered extract is made up to 100 ml with acetic acid. To 1 ml of this soln. is added 9 ml of ceric molybdate reagent and, after 3 to 5 min., the extinction of the red complex is measured at 515 mμ (1-cm cell) against the reagent blank. A correction factor of 1·05 is applied to the value of "free **I**" thus obtained. For **II**, the sample is extracted (Soxhlet thimble) for ≃ 90 min. with ethanol, and the extract is made up to 100 ml. To 1 ml of this soln. is added quickly 9 ml of $K_2Cr_2O_7$ - H_2SO_4 reagent and the extinction of the blue soln. is measured, 3 to 20 min. later, at 575 mμ (1-cm cell) against the reagent blank. Interference by transformation products of **I** is negligible. W. J. BAKER

2700. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1959, **31** (4, Part I), 621–622.—Data applicable to the following determinations are published. **Determination of trace organic impurities in concentrated hydrochloric acid by extraction with carbon disulphide,** H. L. Spell and J. N. Lomonte. **Determination of thionaphthen in naphthalene,** R. E. Seeber and R. G. White. **Determination of phenethyl acetate in phenethyl formate,** A. J. Fenton. **Determination of 4-chloronitrobenzene in 1-chloro-2:4-dinitrobenzene,** R. E. Seeber and B. B. Whitcomb.

See also Abstracts—**2558**, Determination of V in petroleum residues. **2563**, Analysis of sodium sulphide for use in the leather industry. **2807**, A nomographic calculator for organic analysis. **2823**, Gas - liquid chromatography of hydroxyl and amino compounds.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Biological fluids, animal and vegetable tissues

2701. **Problems of quantitative paper chromatography.** Report of meeting of the Association of Clinical Biochemists, October 4, 1958. *Lab. Practice*, 1959, **8** (4), 149–152.—The following are some of the papers read. **Introduction and some theoretical aspects,** R. Consden. **Chromatography of androgens, oestrogens and progesterone,** R. V. Short. **Quantitative chromatography of steroids,** I. E. Bush. **Quantitative measurement of amino-acid paper chromatography,** L. Fowden. **Serum-protein separations on ion-exchange cellulose columns,** H. P. Tombs, K. B. Cooke and N. F. Maclagan. **Uropepsinogen excretion in patients with gastric lesions [Determination of uropepsinogen],** J. Schrager. **Comparison of protein-bound iodine determinations with radioactive-iodine tests in thyroid disease,** K. Steinitz. **The estimation of oxalic acid in urine and other biological material,** A. Hodgkinson and P. M. Zarembski.

2702. **Method of polarographic *in vivo* continuous recording of blood oxygen tension.** F. Kreuzer and C. G. Nessler, jun. (Dartmouth Med. Sch., Hanover, N.H., U.S.A.). *Science*, 1958, **128**, 1005–1006.—Construction of a catheter-type oxygen electrode is described. A continuous tracing of oxygen tension with good reproducibility is obtained.

H. F. W. KIRKPATRICK

2703. **Determination of calcium in biological material.** A. A. Henly and R. A. Saunders (Pathology Dept., Little Bromwich General Hospital, Birmingham, England). *Analyst*, 1958, **83**, 584–586.—Ashed samples of the material are dissolved in small amounts of HCl, the soln. are diluted, the pH is adjusted to $\simeq 5$ with 0·5 *N* NaOH and the vol. is suitably adjusted. Portions (1 ml) of these soln., or of biological fluids (*e.g.*, serum, urine, cerebrospinal fluid), are added to 2 ml of ammonium oxalate - oxalic acid buffer soln. (pH 5) in centrifuge tubes, the liquids are mixed and the tubes are set aside for 30 min. They are then centrifuged and the supernatant liquids are poured off and reserved, if necessary, for the determination of Mg. Each tube is allowed to drain on filter-paper and the ppt. are dissolved in 1-ml portions of 0·2 *N* HCl. A 2-ml portion of EDTA - ethanolamine reagent soln. (prep. described) and 5 drops of indicator soln. (Eriochrome black T in 2-methoxyethanol) are added to each, and the liquids are titrated with standard Mg acetate soln. (5 milli-equiv. per litre) until the colour changes from blue to red. Some samples may require more than the specified vol. of EDTA - ethanolamine reagent to prevent turbidity. Five times the difference between the vol. (ml) of EDTA reagent added and the titre gives the content of Ca (milli-equiv. per litre). The accuracy and precision are good.

A. O. JONES

2704. **Radio-assay of carbon-14 in aqueous solution using a liquid scintillation spectrograph.** D. Steinberg (Nat. Heart Inst., Nat. Inst. of Health, Bethesda, Md., U.S.A.). *Nature*, 1958, **182**, 740–741.—A two-phase system is used. The solid phase consists of small plastic or glass beads which incorporate a fluor (diphenylstilbene), and the liquid phase contains the radioactive material in soln. The beads are packed in a glass tube, into which the test soln. is introduced. The volume of solvent is not critical, provided that the beads are covered, and recovery of the sample afterwards is quantitative.

J. H. WATON

2705. **Determination of zinc by direct extraction from urine with diphenylthiocarbazone.** J. H. R. Kägi and B. L. Vallee (Biophys. Res. Lab., Harvard Med. Sch., Boston, Mass., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1951–1954.—Urine is buffered to pH 5·7 and extracted 4 times with CCl_4 to remove emulsifying substances. Zinc is then extracted to completion with successive portions of 0·003% soln. of dithizone in CCl_4 to a total vol. of 25 ml. The complex is determined by measuring the extinction at 525 and 625 mμ and applying an equation for the mixed colours.

H. F. W. KIRKPATRICK

2706. **Determination of zinc in plant materials using ion-exchange chromatography.** R. H. Maier and J. S. Bullock (Univ. of Arizona, Tucson, U.S.A.). *Anal. Chim. Acta*, 1958, **19** (4), 354–359.—The use of zincon as a colorimetric reagent for Zn requires the preliminary removal of several metals that would interfere. This is accomplished by the use of a column (70 mm high × 13 mm diam.) of Dowex 1-X8, 50 to 100-mesh, anion exchanger. The column is washed free from Zn^{2+} with *N* NaOH and is then treated with 50 ml of 2 *N* HCl. *Procedure*—Dry-ash a sample, containing < 50 μg of Zn, at 475° to 500° for 1 hr. and complete the oxidation by heating with conc. HNO_3 (5 ml), water (5 ml) and $HClO_4$ (70 to 72%, 2 ml) for 1 hr. Finally evaporate to dryness. Dissolve the residue in 10 ml of 2 *N* HCl, filter, and wash the filter with three 5-ml portions of 2 *N* HCl, running the total filtrate directly into the Dowex column. Wash the column with 40 ml of 0·5 *N* HCl. Remove the Zn^{2+} from the column with 30 ml of *N* NaOH. To this eluate add 5 ml of buffer soln., pH 9·0 (Clark and Lubs), and adjust the pH to 9·0 with dil. HCl. Add 1 ml of zincon soln. (0·13 g in 2 ml of *N* NaOH, diluted to 100 ml with water) and dilute to 50 ml. Determine the extinction, within 20 min., at 620 mμ and interpret the result by reference to a calibration curve. Iron is not completely separated if > 600 μg is originally present and interference will then occur.

H. N. S.

2707. **Determination of serum iron and iron-binding capacity.** R. J. Henry, C. Sobel and N. Chiamori (Bio-Science Res. Foundation, Los Angeles, Calif., U.S.A.). *Clin. Chim. Acta*, 1958, **3** (6), 523–530.—A method similar to that of Trinder (*Anal. Abstr.*, 1956, **3**, 3135) is described. This method is adapted to the procedure of Peters *et al.* (*Anal. Abstr.*, 1957, **4**, 3053) for the determination of iron-binding capacity.

H. F. W. KIRKPATRICK

2708. **Spectrophotometric determination of iron in urine using 4:7-diphenyl-1:10-phenanthroline [bathophenanthroline].** M. J. Seven and R. E. Peterson (Nat. Inst. of Arthritis and Metab. Diseases, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2016–2018.—Digest the urine (5 to 10 ml) with conc. H_2SO_4 (0·75 ml) and conc. HNO_3 (5 ml) at approx. 250° until nearly colourless. Wash down the flask with a little H_2O, add 30% H_2O_2 (5 ml) and heat until reaction ceases, cool partially, add 30% H_2O_2 (2 ml) and heat at $\geq$ 250° for 1 hr. Cool partially, wash down the flask with H_2O (20

ml) and add 0·2% $KMnO_4$ soln. dropwise until a faint-pink colour persists (1 to 3 drops). Add 20% hydroxylamine hydrochloride soln. (3 ml), mix, add saturated Na acetate soln. (15 ml) and again mix. Add bathophenanthroline reagent (0·0025 *M* in *iso*amyl alcohol) (4 ml), cover the flask and shake until no further red colour develops (60 to 90 sec.); allow to separate. Draw off the alcoholic soln. and measure the colour at 533 mμ against a reagent blank. The blank, together with standards containing 2 to 4 μg of Fe, is carried through the same process. H. F. W. KIRKPATRICK

2709. **Comparative study of colorimetric methods for the determination of phosphorus. II. Ultraviolet spectrophotometry.** J.-L. Delsal and H. Manhouri (Inst. d'État des Sérums et Vaccins Razi, Hessarek, Iran). *Bull. Soc. Chim. Biol.*, 1958, **40** (7–8), 1169–1177.—Spectrophotometry at 320 mμ when molybdenum blue is extracted with *n*-butanol, or at 340 mμ without extraction, improves the sensitivity of those methods that do not involve heating. [An exception is the method of Berenblum and Chain (*cf. Biochem. J.*, 1938, **32**, 286, 295), in which no increase in sensitivity is obtained.] The effect is independent of the nature of the reducing agent used. In methods carried out after heating and *n*-butanol extraction of the colour, readings at 800 mμ give max. sensitivity. Determination of P as molybdovanadophosphoric acid (Michelsen, *Anal. Chem.*, 1957, **29**, 60) with readings at 315 mμ offers a high degree of sensitivity without the use of a reducing agent. Determination as molybdophosphoric acid at pH 3 can also be effected without a reducing agent by reading at 310 mμ after extraction with *n*-butanol.

III. Determination of orthophosphate in the presence of phosphoric esters (recognised methods). J.-L. Delsal and H. Manhouri. *Ibid.*, 1958, **40** (7–8), 1179–1187.—Reading at 320 mμ improves the sensitivity of the Lowry and Lopez method (*cf. Brit. Abstr. C*, 1946, 286) when carried out at pH 4·0 in the presence of 4×10^{-6} *M* Cu^{2+}. At this concn. of Cu^{2+}, inhibition by Na_2SO_4 ($1·3 \times 10^{-6}$ *M*), cysteine ($0·6 \times 10^{-6}$ *M*), reduced glutathione ($0·6 \times 10^{-6}$ *M*) and $(NH_4)_2SO_4$ (1 ml of a saturated soln. added to a vol. of 6 ml) is suppressed. The sensitivity of the Bruemmer and O'Dell modification of this method (*cf. Anal. Abstr.*, 1956, **3**, 2527) is increased at pH 4·0 by adding 1×10^{-3} *M* Cu^{2+} and reading at 860 mμ. In the Furchgott and Gubareff method (a modification of the Fiske and Subbarrow technique carried out at pH 2·3 in the presence of Cu^{2+}) (*cf. Anal. Abstr.*, 1957, **4**, 1919), the sensitivity is increased fivefold by reading at 320 mμ rather than at 735 mμ but, at this pH, hydrolysis of creatine phosphate is not negligible, thus limiting the usefulness of the method.

IV. Determination of orthophosphate in presence of phosphoric esters (new methods). J.-L. Delsal and H. Manhouri. *Ibid.*, 1958, **40** (11), 1623–1636.—Of four methods critically studied, the following two are recommended. (*i*) *Modified Berenblum and Chain method, at pH 4·0, without extraction*—To 1 ml of tissue extract [prepared with trichloroacetic acid, $HClO_4$ or $(NH_4)_2SO_4$], or 1 ml of blood serum, add 5 ml of acetate buffer (pH 4·0), 3 drops of 40% formaldehyde soln. (to inhibit interference by cysteine and glutathione), 0·5 ml of 5% ammonium molybdate soln. and 0·2 ml of $SnCl_2$ soln. (freshly prepared by dissolving 0·2 g of $SnCl_2.2H_2O$ in 10 ml of water, adding 5 drops of glacial acetic acid, and making up to 100 ml). Shake after each addition, make up to 10 ml with water, and immediately read the extinction in a 1-cm cell at 735 mμ. A blank and a standard containing 10 μg of P are measured at the same time, these containing the amounts of acids or $(NH_4)_2SO_4$ which were contained in the tissue extract. The reaction is immediate, the colour is stable for 15 min., and 1 mg of adenosine triphosphate does not interfere. Amounts of NaF and K oxalate usually used for the deproteinisation of blood serum do not interfere, and hydrolysis of creatine phosphate is negligible under the conditions given. (*ii*) *Determination with metol at pH 4·0 in the presence of $CuSO_4$*—To 1 ml of tissue extract (prepared with $HClO_4$) add 5 ml of acetate buffer (pH 4·0, containing 0·25% of $CuSO_4.5H_2O$), 1 ml of 5% ammonium molybdate soln. and 1 ml of aq. metol soln. (2%, containing 5% of anhyd. Na_2SO_3). Shake after each addition, make up to 10 ml, allow to stand for 2 min., and read the extinction in a 1-cm cell at 880 mμ, a blank and a standard of 10 μg of P being read at the same time. Up to 200 μg of cysteine or glutathione does not interfere, but higher amounts give ppt. or greenish colours; 1 mg of adenosine triphosphate does not interfere, but $(NH_4)_2SO_4$ causes a slow and unstable reaction, and the reaction with trichloroacetic acid is not so rapid as with $HClO_4$. The method is 3·5 times as sensitive as that of Fiske and Subbarow, and can be used for the study of phosphatase activity in acetate, bicarbonate and borate buffers.

D. W. Moss
D. W. Moss
R. E. ESSERY

2710. **Artificially elevated protein-bound-iodine values in blood.** S. F. B. Heijdemann and G. A. Lindeboom (Dept. of Intern. Med., Free Univ., Amsterdam, Netherlands). *Clin. Chim. Acta*, 1958, **3** (6), 565–570 (in English).—Very high values of protein-bound iodine (PBI) occur after cholecystography or during treatment with chlorohydroxyiodoquinoline, and 6 to 12 weeks may elapse before the PBI falls to its normal level. Iodised oil produces raised PBI levels which persist for 1 to 2 years. The effect of compounds used in pyelography usually disappears within 2 weeks.

H. F. W. KIRKPATRICK

2711. **Chemical determination of riboflavine (vitamine B_2) in urine.** B. Gassmann. *Ernährungsforschung*, 1958, **3** (3), 400–413.—Available methods are criticised. An improved method is described which depends on the photochemical conversion of riboflavine into lumiflavine, which is determined fluorimetrically. Preliminary operations are carried out in subdued light with the use of brown-glass vessels. *Procedure*—Add to the sample 3·5 *N* H_2SO_4 (20 ml), heat 50 ml of the mixture in boiling water for 30 min., treat with diastase at 45° and pH 4·5 to 5·4 for 45 min., filter, and extract the filtrate with $CHCl_3$ (non-fluorescing). Transfer several 10-ml aliquots to evaporating dishes; to half the number add 2 ml of a soln. containing 1 μg of riboflavine per ml, and to the other half 2 ml of water. Add to each dish 2 ml of 7 *N* NaOH, and irradiate under an ordinary 500-W lamp at 30 cm distance for 30 to 45 min., keeping the temp. at 20°. Treat the content of each dish with acetic acid (2 ml) and aq. 3% $KMnO_4$ soln. (0·3 ml) for a few minutes, remove excess of $KMnO_4$, and extract separately with $CHCl_3$. Determine the lumiflavine in the (dried) $CHCl_3$ phase of each portion by fluorimetric measurement against standard soln. of fluorescein or quinine sulphate. In the calculation, allowance is made for the added riboflavine and the

blank value of the reagents. The recovery of the added riboflavine as lumiflavine should be 99%. The results agree well with those from microbiological determinations, and show (for 17 samples) a standard deviation of ± 2·4 %. P. S. ARUP

2712. **Extraction technique for estimation of Evans blue [azovan blue] in plasma.** M. Hobsley and E. D. Dew (Dept. of Surg. Studies, Middx. Hosp., London). *J. Clin. Path.*, 1958, **11** (5), 451–454.—The dye is adsorbed on to a cellulose pad which is pulped in normal saline. The cellulose is washed with saline, ether and saline again, extracted with 50% aq. acetone and the colour is read at 610 mμ. The standard is prepared by a similar method. H. F. W. KIRKPATRICK

2713. **Evaluation of glucose determinations in untreated serum samples.** M. Weissman and B. Klein (Vet. Admin. Hosp., Bronx, N.Y., U.S.A.). *Clin. Chem.*, 1958, **4** (5), 420–422.—Fluoride treatment to prevent glycolysis is essential when a delay of an hour or more before analysis is unavoidable. H. F. W. KIRKPATRICK

2714. **Diagnostic composition.** Miles Laboratories, Inc. Brit. Pat. 811,938; date appl. 31.8.55.—This patent is an extension of Brit. Pat. 575,612 and 615,659 covering tablets for use in the determination of glucose in body fluids. The use of additional organic acids to produce the necessary heat with the NaOH present is claimed. These are used in combination with a complexing agent for the Cu such as a tartrate, citrate or a mixture of EDTA and triethanolamine. N. E.

2715. **Determination of heparin.** M. Herbain (Services de Recherches Roussel-Uclaf, Romainville, Seine). *Bull. Soc. Chim. Biol.*, 1958, **40** (7–8), 1221–1235.—Improvements in a method based on the coagulation rate of oxalated plasma in the presence of thrombin and heparin are described. Bovine plasma, purified by three treatments with pptd. $BaSO_4$ (0·1 g per ml) by centrifugation and decantation, is used with thrombin from the same source. The reaction is carried out in a tube with a side-arm, the plasma being placed in the main limb and the thrombin - heparin mixture in the side-arm. After mixing the reactants, the increase in opacity is observed in a photometer, the time taken to reach an arbitrary value being regarded as the coagulation time. The result obtained with an unknown amount of heparin is compared with a standard curve. The use of purified plasma and photometric estimation of increase in opacity improves the reproducibility of the results, though some specimens of plasma fail to show a measurable increase in opacity on coagulation and must be discarded. D. W. Moss

2716. **Problems of porphyrin analysis.** A. M. Dancewicz and O. Gutniak (Dział Ochrony Zdrowia Inst. Badań Jądrowych PAN, Warszawa, Poland). *Chem. Anal., Warsaw*, 1958, **3** (2), 99–105.—Methods for the determination of coproporphyrin (**I**) and uroporphyrin (**II**) in human urine are discussed, and a simple procedure for **I**, based on the method of Schwartz *et al.* (*cf. Brit. Abstr. C*, 1951, 461), has been developed. Extract 30 ml of urine, buffered with acetic acid - satd. Na acetate soln. (4:1), with ethyl acetate. Repeat the extraction of the aq. layer, wash the combined extracts with 1% Na acetate soln. (2 × 50 to 60 ml), then shake with 0·005% iodine soln. (15 ml). Extract **I** from this soln. with 10-ml portions of 5% HCl until the red fluorescence is discharged, then determine **I** spectrophotometrically. To determine **II**, extract the sample (maintained at pH 3·0 to 3·2 with HCl) with ethyl acetate, then re-extract with 2% HCl, and measure spectrophotometrically. Alternatively, extract the sample with ether, and to the aq. layer add a little Pb acetate; set aside for 30 min., filter and dissolve the ppt. in 25% HCl. Determine **II** spectrophotometrically; corrections are necessary.

S. WASILEWSKI

2717. **Arbutin in *Pyrus communis*.** L. Zechner and M. Vrba (Pharm.-chem. Inst., Univ. Graz, Austria). *Sci. Pharm.*, 1958, **26** (3), 145–163.—A description is given of Zechner's method for the determination of arbutin in the leaves, as modified by Grimme (*cf. Pharm. Zentralh.*, 1933, **74**, 559). The determination must be made either on fresh leaves or on leaves which have been dried *in vacuo* at room temp.; considerable losses of arbutin occur on air-drying the leaves or on drying at 70°. A method for obtaining pure arbutin from the leaves of *P. communis* by extraction with anhyd. ethanol is described. Data are given for the seasonal variations of the arbutin content in the leaves; the maximum content (0·27 to 0·29%) occurs in late August. P. S. ARUP

2718. **The determination of formaldehyde and acetaldehyde liberated in the periodate and ninhydrin reactions.** S. L. Tompsett (Northern Gen. Hospital, Edinburgh, Gt. Britain). *Anal. Chim. Acta*, 1958, **19** (4), 360–363.—When the reactions named give rise to both formaldehyde and acetaldehyde (as with certain biological samples), separation of these aldehydes is necessary as a preliminary to their separate determination with chromotropic acid and *p*-hydroxydiphenyl, respectively. The separation is accomplished by the aeration technique of Cox (*Brit. Abstr. C*, 1952, 555). The samples are oxidised by a procedure described previously (*cf.* Smith and Tompsett, *Anal. Abstr.*, 1954, **1**, 773). H. N. S.

2719. **Isolation of amino acids from a small amount of hydrolysed protein.** E. F. Efimochkina. *Vopr. Med. Khim.*, 1958, **4** (4), 309–314; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (4), Abstr. No. 3350.—Aromatic dicarboxylic acids and the principal amino acids are obtained from a protein hydrolysate (0·5 to 1 g) by adsorption on to super-activated carbon or aluminium oxide. This method is recommended for the isolation, from tissue proteins, of pure amino acids intended for the analysis of stable or radioactive isotopes when a partition column (ion-exchange chromatography) cannot be used.

K. R. C.

2720. **Determination of the principal amino acids in protein hydrolysates.** V. K. Orlov. *Trudy Khim. Prirod. Soedinen. Kishinevsk. Univ.*, 1958, (1), 97–102; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (4), Abstr. No. 3351.—A method is described for the group isolation of amino acids and for the determination of the principal amino acids of the acid hydrolysate of casein by means of adsorption on to a carbon column and a cationite column. The preparation of the adsorbent is described.

K. R. C.

2721. **Determination of N-carbamoyl derivatives of amino acids by means of diacetyl monoxime.** R. Crokaert and E. Schram (Lab. de Biochim., Fac. de Méd., Univ. Libre, Bruxelles). *Bull. Soc. Chim. Biol.*, 1958, **40** (7–8), 1093–1105.—The factors that affect colour development in the method of Koritz and Cohen (*cf. Anal. Abstr.*, 1954, **1**, 2760) have been studied, and a standardised procedure is recommended. The reaction is carried out in a soln. of diphenylamine-*p*-sulphonic acid in 0·1 *N* HCl; heating for 10 min. in the boiling-water bath before addition of $K_2S_2O_8$ gives optimum colour development. After addition of $K_2S_2O_8$, the temp. must be controlled very carefully to obtain reproducible results. A temp. of 25° is recommended. At higher temp., max. colour is more intense and is attained more rapidly, but the colour deteriorates more quickly. Stabilisation of the colour is favoured by addition of ethanol (1 ml). Increasing the concn. of $K_2S_2O_8$ produces an effect similar to that of increased temp. Exposure to direct light, which causes a change in the characteristic colour and an increase in blank values, must be avoided. Absorption spectra of various derivatives are closely similar, with max. near 560 mμ. The Beer - Lambert law is not obeyed for optical densities above 0·50, and a standard curve must be constructed. An enhancement of the colour of the N-carbamoylglutamic acid derivative in the presence of taurine and ornithine has been observed. The colour of this derivative is inhibited by addition of cysteine, inhibition being prevented by excess of $K_2S_2O_8$. The action of cysteine may be due to its oxidation, leaving little of the $K_2S_2O_8$ to take part in colour development (other reducing substances which may be present probably act similarly). The method has greater sensitivity than those previously described. D. W. Moss

2722. **Assignments of the vibrational frequencies of glycine.** Masamichi Tsuboi, Takaharu Onishi, Ichiro Nakagawa, Takehiko Shimanouchi and Sanichiro Mizushima (Tokyo Univ., Japan). *Spectrochim. Acta*, 1958, **12** (2–3), 253–261.—Assignments based on spectra, recorded between 1800 cm^{-1} and 400 cm^{-1}, of α-glycine, [D_2]-α-glycine, glycine hydrochloride, [D_5]glycine hydrochloride, Na glycinate, and Na chloroacetate, and dichroic measurements on the single crystal of γ-glycine are given. E. G. Cummins

2723. **Use of the tandem-transfer technique in the rapid separation on ion-exchange resin papers of phenylalanine and tyrosine from mixtures of amino acids.** M. M. Tuckerman, R. A. Osteryoung and F. C. Nachod (Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 251–255.—A study of the R_F values of several amino acids on an experimental Amberlite IRC-50 (H) resin-impregnated paper suggested that a mixture of lysine, phenylalanine, tyrosine and leucine would give two broad bands, one containing lysine and phenylalanine and the other tyrosine and leucine. By using a composite strip made up of 2·5 cm of IR-120 (Na) resin paper followed by 19·5 cm of IRC-50 (H) resin paper, good separation into four zones may be readily obtained under the conditions used by Tuckerman (*Anal. Abstr.*, 1958, **5**, 2338). The two papers are joined with cellulose tape, overlapping about 2 mm at the join. T. R. Andrew

2724. **Micro-determination of half-cystine residues in proteins.** Shiro Akabori and Teruko Fujiwara (Inst. Protein Res., Osaka Univ., Japan). *Bull. Soc. Chim. Biol.*, 1958, **10** (12), 1983–1992 (in English).—The apparatus used (illustrated) is a modification of that previously described (*cf.* Kuratomi *et al.*, *Anal. Abstr.*, 1958, **5**, 2742). The method depends on the fact that both the disulphide and sulphydryl sulphur can be converted into H_2S by heating proteins with hydrazine; methionine or taurine sulphur is not attacked. The sample (containing 30 to 100 μg of half-cystine) is heated to 120° to 130° for 5 hr. with 0·5 ml of hydrazine hydrate. The product is diluted with 0·01 *N* NaOH so as to contain 4 to 20 μg of H_2S per ml. The H_2S is distilled into Zn acetate soln. and determined colorimetrically by Caro's reaction in which methylene blue is produced from H_2S with *p*-aminodimethylaniline. N. E.

2725. **Voltammetric determination of histidine.** B. Jaselskis (Dept. of Chem., Univ. of Michigan, Ann Arbor, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1968–1971.—Histidine is determined by titration with cobaltous sulphate soln. at the dropping mercury electrode, with the anodic wave at − 0·20 V *vs.* the S.C.E. The method is specific for free histidine, and its application in the presence of other amino acids, histamine and protein hydrolysates is described. H. F. W. Kirkpatrick

2726. **Catalytic effect of thyroxine, 3:5:3′-triiodothyronine, 3:5-di-iodothyronine and 3:5-di-iodotyrosine on the reduction of ceric ammonium sulphate by arsenous acid in the presence of chloride.** G. Morreale de Escobar and E. Gutiérrez Rios (Dept. of Inorg. Chem., Univ. of Granada, Spain). *Clin. Chim. Acta*, 1958, **3** (6), 548–556 (in English).—The reaction is catalysed by each of these compounds and proceeds according to first-order kinetics. Aq. soln. containing concn. of the compounds of the order of 10^{-7} *M* may be assayed by this means. H. F. W. Kirkpatrick

2727. **The biosynthesis of spermidine and spermine from putrescine and methionine. [Determination of putrescine, spermidine and spermine.]** H. Tabor, S. M. Rosenthal and C. W. Tabor (Nat. Inst. of Arthritis and Metabolic Diseases, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1958, **233** (4), 907–914.—Chromatographic methods are described for the determination of these diamines in bacterial and tissue extracts. The best separation of these diamines from each other and from contaminating amino acids is obtained with the resin Amberlite XE-64 in the K form. When trichloroacetic acid extracts are assayed, the acid is first removed by extraction with diethyl ether and the aq. soln. is then adjusted with KOH to pH 7. The diamines are obtained by gradient elution with a solution of pH 7·2 containing 0·1 *M* Na_2HPO_4 and 1·67 *M* Na_2SO_4, and are extracted from the eluates (after addition of excess of Na_2PO_4) with *n*- or *tert.*-butanol. Each diamine is then determined colorimetrically by the fluorodinitrobenzene method. The eluates obtained in this separation contain large amounts of salts and the following modifications are more suitable for radioactive-labelled diamines. Dowex-50 (H form) columns are used for the separation and gradient elution is effected with 2·5 *N* HCl. This method does not separate putrescine from amino acids, and does not satisfactorily separate spermine or spermidine from S-adenosylmethionine. This last-named separation is effected, after the soln. is neutralised with KOH to pH 7, by adsorption on Amberlite XE-64 (H form) and elution with *N* acetic acid. J. N. Ashley

2728. **Assay of urinary peptides using a biuret reagent.** B. Balikov, E. R. Lozano and R. A. Castello (Walter Reed Army Med. Centre, Washington, D.C., U.S.A.). *Clin. Chem.*, 1958, **4** (5), 409–419.—Variations in results due to the biuret reagent have been investigated. Its use and limitations are more clearly defined.

H. F. W. KIRKPATRICK

2729. **Investigation of pre-albumin in serum. I. Electrophoretic demonstration of pre-albumin on filter-paper and its quantitative variation.** F. W. Aly and K. H. Niederhellmann (Med. Univ.-klinik, Marburg a.d. Lahn, Germany). *Klin. Wochschr.*, 1958, **36** (20), 954–959.—Electrophoresis of the serum (0·1 ml) is carried out with a barbitone buffer (pH 8·6, μ 0·06) and a p.d. of 90 V for 24 hr. The strips are stained with 1% bromophenol blue soln. in 70% ethanol saturated with $HgCl_2$ and containing 1% of acetic acid, and are then washed with 0·5% acetic acid. The protein fractions are eluted with 0·01 *N* NaOH (60 min.) and the soln. are read at 570 mμ. Results with normal and pathological sera are tabulated. H. F. W. KIRKPATRICK

2730. **Determination of serum albumin by the method of isotope dilution.** J. Hradec (Biochem. Dept., Onkolog. Inst., Prague). *Chem. Listy*, 1958, **52** (10), 2015–2017.—Serum albumin (**I**) can be pptd. with trichloroacetic acid, extracted into an organic solvent and then determined by the method of isotope dilution with the use of radioactive serum albumin (^{35}S). *Procedure*—To the sample containing about 1 to 3 mg of **I** in the presence of an excess of other albumins add a soln. of radioactive **I** (0·1 ml) (4·8 to 9·6 mg in 1 ml; specific activity 0·4 to 0·5 μC per mg) and trichloroacetic acid (30%) to 5% concn. Mix, set aside for 10 min. and separate the ppt. by centrifuging. Homogenise the separated ppt. with ethanol (2 ml). Repeat the centrifuging and separate the supernatant liquid containing the extracted albumin. Add ether (2 ml) and mix till a turbidity appears. Set aside for 20 min., separate the ppt. by centrifuging and wash it with ether (2 ml). Homogenise with ether and measure the radioactivity of the ppt. on weighed filters. Compare with a calibration curve prepared with the use of radioactive **I**. The accuracy is $\pm$ 2%. J. ZÝKA

2731. **Determination of serum lipoproteins by paper electrophoresis after preliminary staining with Sudan black B.** E. L. Kanabrocki, E. Kaplan, D. S. Kinnory, A. A. Imperato, J. E. Berry and L. A. Baker (Vet. Admin. Hosp., Hines, Ill., U.S.A.). *Clin. Chem.*, 1958, **4** (5), 382–391.—A modification of the method of Macdonald and Bermes (*Clin. Chem.*, 1956, **2**, 257) is described, the serum being pre-stained before electrophoresis.

H. F. W. KIRKPATRICK

2732. **Specific determination of creatinine and creatine by the Sakaguchi reaction after oxidation by Nessler reagent.** J. Chazerain (Lab. de Pharm., l'Hôpital de Boucicaut, Paris). *Ann. Pharm. Franç.*, 1958, **16** (6), 413–421.—Creatinine is oxidised by alkaline Nessler reagent in the cold and the oxalylmethylguanidine formed does not give a colour with Sakaguchi reagent, but is converted almost instantaneously on heating on a water bath to methylguanidine which does give the Sakaguchi reaction. Creatine does not reduce Nessler reagent in the cold, but does so rather slowly on heating in alkaline soln. The possible analytical applications of these reactions are discussed. In biological materials it is not possible to determine creatine and creatinine separately as can be done with pure soln., and only the creatinine can be determined since the heating in alkaline soln., necessary to oxidise the creatine, interferes with the Sakaguchi reaction for such mixtures. *Procedure for creatinine in biological fluids*—Blood (NaF, and not oxalate, must be used as anticoagulant) or serum or urine diluted 400 times is treated with Na_2WO_4 to remove protein, and the centrifugate (2 ml) is treated with 0·2 ml of iodomercurate reagent (HgI_2 0·36 g, NaI 2·6 g, and H_2O to 100 ml) and 0·25 ml of 1·25 *N* NaOH. After 15 min. at room temp., 0·5 ml of a phosphate buffer is added, and the soln. is heated for exactly 10 min. on a water bath. The Sakaguchi reagent [0·20 ml of a mixture of equal parts of 0·1% 1-naphthol soln. (freshly diluted with water from a 1% ethanolic soln.) and 10% EDTA soln; 0·4 ml of hypobromite soln. made by dissolving 0·8 ml of Br in 100 ml of NaOH soln. (1:4), is added with immediate stirring] is added to the cooled soln. and 2 min. later 0·1 ml of 5% $Na_2S_2O_3.5H_2O$ soln. The extinction is measured at 520 mμ. Blanks and standards are treated similarly. E. J. H. BIRCH

2733. **Method for the determination of cholesterol in blood serum.** L. Klungsöyr, E. Haukenes and K. Closs (Biochem. Lab., Haukeland Sykehus, Bergen, Norway). *Clin. Chim. Acta*, 1958, **3** (6), 514–518 (in English).—To serum (0·2 ml) in a centrifuge tube add ethyl acetate - 96% ethanol (1:1) (5 ml), stopper the tube with a cork covered with thin Cellophane, shake and centrifuge for 10 min. To an aliquot (1 ml) of clear extract add ethyl acetate (5 ml) and then iron reagent (1 ml of 10% $FeCl_3$ in glacial acetic acid diluted to 100 ml with conc. H_2SO_4) (4 ml) so as to form two layers. Mix the layers by rotating, allow to cool (about 30 min.) and read at 490 mμ. Prepare a standard by treating 1 ml of a soln. of cholesterol (10 mg per 100 ml) in the solvent similarly, and a blank with the solvent alone. The method gives reproducible results approx. 14% higher than those given by the Schloenheimer and Sperry method.

H. F. W. KIRKPATRICK

2734. **Determination of free and esterified cholesterol after separation by paper chromatography.** A. Holasek, H. Lieb and I. Schaar (Med.-Chem. Inst., Univ. Graz). *Klin. Wochschr.*, 1958, **36** (20), 942–944.—Lipids are extracted from serum with acetone - 95% ethanol (1:1) and the residue from evaporation of the solvent is dissolved in a little toluene. This soln. is applied to paper impregnated with a 10% soln. of liquid paraffin in light petroleum and chromatographed with *iso*propyl alcohol - methanol - H_2O (9:5:6) as solvent. The esterified cholesterol remains at the point of application whilst the free steroid moves with the solvent (R_F 0·35 to 0·40). The appropriate portions of the strip are cut out, the steroid is eluted with benzene and determined by the Liebermann - Burchard reaction after removal of the solvent.

H. F. W. KIRKPATRICK

2735. **17-Oxosteroid determination in urine. III. Column chromatographic fractionation method of Johnsen.** H. Zimmermann, W. Staib and H. Pelzer (Physiol.-Chem. Inst. d. Med. Akad., Düsseldorf, Germany). *Klin. Wochschr.*, 1958, **36** (20), 982–984.—The Al_2O_3 column method of Johnsen

(*Acta Endocr., Copenhagen*, 1956, **21**, 127) is extended. Additional elution with 0·4 or 0·5% ethanol in benzene yields the clinically important 11-oxosteroids, which can be determined quantitatively. The method is suitable for routine analyses.
H. F. W. KIRKPATRICK

2736. **Determination of dehydro*epi*androsterone in urine.** M. F. Jayle and D. Malassis (Lab. de Chimie Biol., Fac. de Méd., 45 Rue des Saints-Pères, Paris). *Bull. Soc. Chim. Biol.*, 1958, **40** (9–10), 1349–1373.—The urine is adjusted to pH 4·7 with acetic acid and one-third of its volume of acetate buffer (1·0 *M*, pH 4·7) is added. Hydrolysis is carried out in the autoclave at 120° for 1 hr. The liberated dehydro*epi*androsterone (**I**) is extracted into freshly distilled ether and reduced to dryness. The volume is made up to 5 ml with ethanol and the Zimmermann reaction is carried out. The colour is extracted into ether and its extinction determined at 440, 520 and 600 mμ. The readings are corrected according to Allen's equation, and compared with a standard curve. Normal values given by the method are—males, 1·8 mg per 24 hr. (standard deviation ± 0·75, 40 determinations); females, 1·0 mg per 24 hr. (standard deviation ± 0·40, 56 determinations). For best accuracy, a sample volume containing 20 to 100 μg of **I** is recommended. Paper chromatography has been used to show that **I** forms nearly all of the 17-oxosteroid liberated by this hydrolysis technique, and hydrolysis is quant. up to 200 μg of **I** per litre. Concentrations of **I** down to 30 μg per litre can be detected. A 70% recovery of added **I** can be achieved by hydrolysis for 1 hr. at 120°; this can be increased to 85% by hydrolysis for 4 hr. at 100°. The error of duplicate determinations is 2·5%. Reasons for the choice of the Zimmermann reaction and of the hydrolysis conditions stated, and proof that **I** is excreted entirely in the sulpho-conjugated form, are discussed. D. W. Moss

2737. **Micro-determination of testosterone in human spermatic vein blood.** N. Hollander and V. P. Hollander (Dept. of Med. and Biochem., Univ. of Virginia, Charlottesville, U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1958, **18** (9), 966–971.—Plasma is extracted with ether and partitioned between light petroleum and 70% ethanol. The alcoholic fraction is treated with 2:4-dinitrophenylhydrazine and the derivative is chromatographed on two different columns to const. specific activity.
H. F. W. KIRKPATRICK

2738. **Quantitative determination of pepsin by paper chromatography.** M. Kopitar, D. Lebez and S. Klemenc-Šebek. *Rep. "J. Stefan" Inst.*, 1958, **5**, 133–136.—Haemoglobin (0·5 ml of 4% aq. soln.) and 0·1 *N* HCl (0·5 ml) were placed in a 2-ml test-tube, kept for 5 min. at 100° and cooled. Pepsin was tested within the range 10 to 100 μg per ml. Hydrolysis was carried out at 38° and after 15 min. stopped by heating to 100° for 10 min. The hydrolysate (5 μl) was chromatographed and the spots were detected with ninhydrin followed by the copper reagent of Bode *et al.* (*Brit. Abstr. C*, 1953, 214). The chromatogram was evaluated by means of a double-beam recording and integrating reflectance densitometer. N. E.

2739. **Serum trypsin: a new diagnostic test for pancreatic disease.** G. L. Nardi and C. W. Lees (Dept. Surgery, Harvard Med. School, Boston, Mass.). *New Eng. J. Med.*, 1958, **258** (16), 797–798.—Trypsin rapidly hydrolyses the synthetic polypeptide amide, α-benzoyl-L-argininamide hydrochloride, to benzoyl-L-arginine and ammonia, and the rate of hydrolysis is proportional to the enzyme concentration. The patient's serum is treated with the substrate at an unspecified temperature for a period of 1 hr., and the ammonia formed is estimated by a modified Conway micro-diffusion technique. Commercial lyophilised trypsin is used as a standard. The substrate is thought to be specific for trypsin in blood serum. R. A. BRENAN

2740. **Serum amylase activity, its determination in health and in diabetes mellitus.** H. V. Street (Crumpsall Hosp., Manchester, England). *Clin. Chim. Acta*, 1958, **3** (6), 501–513.—The method of Street and Close (*Anal. Abstr.*, 1957, **4**, 2346) showed no significant difference in enzyme activity in normal and diabetic patients. The saccharogenic method of Somogyi gives misleading results when the blood sugar level is > 150 mg per 100 ml.
H. F. W. KIRKPATRICK

2741. **Stability of lactic dehydrogenase in serum.** J. A. Lazaroni, jun., E. C. Maier and L. R. Gorczyca (Clin. Lab., San Bernardini, Calif., U.S.A.). *Clin. Chem.*, 1958, **4** (5), 379–381.—The enzyme is stable for at least 8 days at 25° and 7 days at 37°. Transported specimens are therefore usually suitable for this determination.
H. F. W. KIRKPATRICK

2742. **Estimation of high concentrations of plasma acid phosphatase.** E. Bowers and K. W. Denson (Dept. of Clin. Path., St. Pancras Hosp., London). *J. Clin. Path.*, 1958, **11** (5), 448–450.—Dilution of densely coloured soln. with Folin - Ciocalteu reagent, Na_2CO_3 soln. and H_2O so as to increase the concn. of these reagents in the final soln. extends the range of linear colour development from 30 to 300 units in comparison with dilution with H_2O.
H. F. W. KIRKPATRICK

2743. **Sources of variation in a standardised and a semi-micro procedure for the spectrophotometric assay of serum glutamic - oxalacetic transaminase concentrations.** A. J. Schneider and M. J. Willis (Lab. Branch, Communicable Dis. Centre, Atlanta, Ga., U.S.A.). *Clin. Chem.*, 1958, **4** (5), 392–408.—The errors and variations with temp. of the methods described, and a standard unit of transaminase activity, are defined. H. F. W. KIRKPATRICK

See also Abstracts—**2489**, Determination of Mg in plant ash. **2493**, Determination of Sr in plant ash. **2598**, Determination of Mn in seaweed, **2640**, Spray for chromatograms of reducing sugars, **2641**, Determination of reducing sugars. **2671**, Determination of benzimidazolone in plasma. **2750**, Determination of diosgenin in *Dioscorea*. **2772**, Determination of the Sr to Ca ratio in blood. faeces and urine. **2803**, Determination of parathion in biological products. **2810**, Calibration of Warburg manometers.

Pharmaceutical analysis

2744. **Paper chromatography of poppy alkaloids. III. Quantitative determination of six principal alkaloids of poppy, opium and their preparations.** R. Miram and S. Pfeifer (Pharm. Inst., Humboldt Univ., Berlin). *Sci. Pharm.*, 1958, **26** (3), 153–167.—The alkaloids are separated from opium and its preparations by extraction with 0·5 *N* H_2SO_4 and filtration; from the capsules (dried and pulverised) they are separated by moistening with aq. Na_2CO_3 soln. and extraction of the mass with a mixture of dichloromethane, ether and methanol (6:3:1), the extract being slowly filtered through a layer of anhyd. Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue is dissolved in ether, and the soln. is extracted with 0·5 *N* H_2SO_4; the acid soln. is treated with trichloroacetic acid and filtered. A slightly modified procedure is used for dealing with other plant parts. The alkaloids in the acid soln. are separated into two fractions as follows: after adjustment of the soln. to pH 8·1 to 8·4, the codeine, thebaine, narcotine and papaverine (group *A*) are extracted by $CHCl_3$, and most of the morphine and narcotoline (group *B*) is retained in the aq. phase. The $CHCl_3$ extract also includes part of the morphine and narcotoline; these are removed by extraction with 0·1 *N* NaOH, and the aq. phase is combined with that from the previous extraction. The morphine and narcotoline are extracted from the aq. phase (adjusted to pH 7·8 to 8·1) by extraction with a mixture of $CHCl_3$ and *iso*propyl alcohol (3:1); these two alkaloids are chromatographically resolved on paper buffered at pH 4·0 with water-saturated *n*-butanol as ascending solvent. The alkaloids of group *A* are resolved by a process of "double chromatography." A strip of paper is folded into the shape of a narrow V, and suspended so that the apex will dip into the solvent. One arm of the V is buffered at pH 4·0, and the narcotine and papaverine are resolved along this arm with water-saturated ether as ascending solvent. Thebaine and codeine remain at the starting point. The arm of the V containing the narcotine and papaverine is cut off just above the starting point, the remaining strip is buffered at pH 5·5, and the thebaine and codeine are resolved with water-saturated *n*-butanol as solvent. The alkaloid spots on the chromatogram are made visible by a modified Dragendorff reagent, and optically evaluated on a photographic film negative by a previously described technique (*cf. Pharm. Zentralh.*, 1957, **96**, 457). The range of the determination is 30 to 100 μg of morphine or narcotoline, and 10 to 70 μg for the other alkaloids. The limits of accuracy are 5 to 10%. P. S. ARUP

2745. **The harmful effect of autoxidised ether in the analysis of alkaloids and other organic bases. II. Determination of alkaloids in extract of nux vomica.** B. Samdahl and E. H. Vihovde (Lab. de Chim. Pharm., Inst. Pharm., Univ. Oslo). *Medd. Norsk Farm. Selsk.*, 1958, **20** (10), 167–176.—Paper chromatography and potentiometric titrations are used to show that the presence of > 0·01% of peroxides in the ether used for extraction leads to conversion of brucine and strychnine into the N-oxides, which are much weaker bases than the parent alkaloids. A. R. ROGERS

2746. **Determination of strychnine in nux vomica by paper chromatography.** G. P. Briner (Dept. of Pharmacol., Univ. of Melbourne, Australia). *Nature*, 1958, **182**, 742.—Dissolve the extracted alkaloids in $CHCl_3$ and apply an aliquot containing 20 to 60 μg of strychnine to Whatman No. 1 paper. Develop by the ascending technique with *n*-butanol - *n*-propanol - 0·05 *N* HCl (1:2:1). Dry the paper and use u.v. photography to reveal the positions of the spots. Elute the cut paper with H_2O and measure the extinction at 255 mμ.

A. R. ROGERS

2747. **The reserpine, rescinnamine and deserpidine content of rauwolfia root.** D. Banes, A. E. H. Houk and J. Wolff (Div. Pharm. Chem., Food and Drug Admin., Washington, D.C.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (9), 625–627.—The reserpine - rescinnamine group of alkaloids was extracted by the method of Banes *et al.* (*cf. Anal. Abstr.*, 1957, **4**, 1324). The alkaloids were determined by the nitrite method of Banes (*loc. cit.*) and also were separated and determined individually by the method of Hayden *et al.* (*cf. Anal. Abstr.*, 1958, **5**, 4276). The two sets of values for the analysis of powdered roots showed good correlation, but the results by the nitrite method were about 15% higher, presumably because of the inclusion of a small quantity of other chromogenic alkaloids.

A. R. ROGERS

2748. **Modification of the method of isolating veratrine from biological materials.** E. A. Bolkova and T. V. Marchenko. *Trudy Kharkovsk. Farmatsev. Inst.*, 1957, (1), 115–118; *Ref. Zhur., Khim., Biol. Khim.*, 1959, (4), Abstr. No. 3424.—Veratrine (**I**) was extracted with $CHCl_3$ from an aq. soln. in the presence of tartaric acid. With an increase in the tartaric acid concn., the hydrolysis of **I** and its extraction by $CHCl_3$ was found to be reduced. It is recommended that this be made use of in order to reduce the loss of **I** during its isolation from biological materials in forensic laboratories.

K. R. C.

2749. **A note on the assay of digitoxin preparations.** D. Banes, A. E. H. Houk and J. Wolff (Div. Pharm. Chem., Food and Drug Admin., Washington, D.C.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (9), 686.—Analysis of 8 samples of digitoxin powder and 21 lots of tablets shows that the methods of the U.S.P. XV and the A.O.A.C. (*cf. J. Ass. Off. Agric. Chem.*, 1958, **41**, 56) yield concordant assay values.

A. R. ROGERS

2750. **Assay of *Dioscorea prazeri* and *D. deltoidea* for diosgenin.** R. N. Chakravarti and S. N. Dash (Dept. of Chem., School of Tropical Medicine, Calcutta). *J. Instn Chem., India*, 1958, **30** (5), 269–271.—Diosgenin is determined in tubers of species of *Dioscorea* by extracting the dried powdered material with ether, heating the residue at 50° to remove ether, and extracting with 90% ethanol; the extract is freed from ethanol and dissolved in water, HCl and benzene are added, and the mixture is heated under reflux with benzene; the saponin is hydrolysed to yield sapogenin, which passes into the benzene layer. This layer is removed, and the process is repeated twice with fresh benzene. Benzene is removed from the combined extracts, the residue is dissolved in ether, washed alternately with 5% NaOH soln. and water (× 4), freed from ether, dried at 100°, washed with acetone, dried again, and weighed. Mean yields of diosgenin were 2·48 and 2·15% for two samples of *D. prazeri*, and 4·36 and 4·03% for two samples of *D. deltoidea*.

M. D. ANDERSON

2751. **Carbamate-ammonia assay for novobiocin.** F. A. Bacher, G. V. Downing, jun., and J. S. Wood, jun. (Merck, Sharp & Dohme Res. Lab., Rahway, N.J., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1993–1995.—The sample (0·09 millimole) is heated for 10 min. with 2 *N* NaOH (5 ml) in a modified Kjeldahl distillation apparatus at b.p. without appreciable distillation, any distillate being trapped in 2% boric acid soln. (20 ml); 6 *N* H_2SO_4 (2 ml) is then added with continued heating and when the soln. is thoroughly mixed 2 *N* NaOH (5 ml) is run in. The distillate (30 ml) is then collected and titrated with 0·01 *N* HCl, a mixed indicator (0·1% ethanolic methyl red - 0·1% ethanolic bromocresol green, 1:5) being used. The procedure is rapid and the precision is within ± 1%. Good agreement was obtained with microbiological assay.

H. F. W. KIRKPATRICK

2752. **Application of ethylenediaminetetra-acetate titration to the determination of zinc in zinc bacitracin.** J. L. Charles and P. J. Weiss (Food and Drug Admin., Washington, D.C., U.S.A.). *Antibiot. & Chemother.*, 1958, **8** (10), 496–499.—The procedure described is more rapid than the official 8-hydroxyquinoline method and gives comparable results; Ca^{2+} and Mg^{2+} interfere. The Zn is determined by titration with EDTA (disodium salt), with Eriochrome black T as indicator.

W. H. C. SHAW

2753. **Microbiological assay for panthenol in pharmaceutical vitamin products.** O. D. Bird and L. McCready (Res. Div., Parke, Davis & Co., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2045–2046.—The proposed method is based on the inhibition of growth of *Leuconostoc mesenteroides* under standard conditions. Application may be made without prior treatment to all types of vitamin preparations, and hydrolytic products of panthenol (**I**) do not interfere. Pantothenic acid (**II**) is easily removed immediately before assay by shaking the diluted sample (containing ≃ 100 μg of **I** and 0·5 μg of **II** per 100 ml) with Amberlite resin MB-1 (2·5 g), allowing the resin to settle, and adding the supernatant fluid to the assay tubes.

H. F. W. KIRKPATRICK

2754. **Quantitative studies of scopoletin in cigarette smoke and tobacco.** Chao-Hwa Yang, Yasushi Nakagawa and S. Wender (Chem. Dept., Univ. of Oklahoma, Norman, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2041–2044.—Accurate determination is complicated by the presence of many interfering substances with only a small amount of scopoletin, and in the method described these are eliminated by repeated paper chromatography with different solvent systems. The final determination is made by measuring the u.v. extinction at 344 mμ. Results with various samples of tobacco and cigarette smoke are tabulated. An average survival in the smoke of about 20% was found, the average total scopoletin content of the tobacco being about 10 mg per 100 g. H. F. W. KIRKPATRICK

2755. **Detection of some drugs by "test-tube" chromatography. I. Analgesics (opium alkaloids, their derivatives and synthetic substances). II. Local anaesthetics.** R. Fischer and N. Otterbeck (Univ. Graz, Austria). *Sci. Pharm.*, 1957, **25** (4), 242–248; 1958, **26** (2), 76–78.—Apparatus suitable for qualitative "test-tube" paper chromatography is described (*cf.* Gorbach *et al.*, *Anal. Abstr.*, 1956, **3**, 1927). The four solvent systems recommended for the separation of 19 analgesic and 13 local anaesthetic drugs are *n*-butanol - water (4:1), water-saturated *n*-butanol - acetic acid (10:3), butyl acetate - *n*-butanol - acetic acid - water (85:15:40:22), and butyl acetate - *n*-butanol - *iso*butyl alcohol - acetic acid - water (2:1:1:2:3). Tables of R_F values are given.

III. Barbiturates, some antithyroid substances, phenothiazines and stimulants. R. Fischer and N. Otterbeck. *Ibid.*, 1958, **26** (3), 184–191.—The R_F values and the appropriate solvents and reagents are given for 19 barbiturates, 6 antithyroid substances, 8 phenothiazines and 7 stimulants. The tests can be completed within 4 hr., and are sensitive to ≃ 5 μg of substance. A. R. ROGERS

P. S. ARUP

2756. **Principles in the spectrophotometric determination of propoxycaine in the presence of procaine.** E. G. Feldmann, W. Mahler and H. M. Koehler (Div. of Chem., Amer. Dental Ass., Chicago, Ill.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (9), 676–680.—Propoxycaine (**I**) is determined by its strong u.v. absorption at 300 mμ in 2 *N* HCl, with little interference by procaine (**II**). Total anaesthetic concn. in soln. containing **I** plus **II** is determined by the absorption at 305 mμ in aq. soln.

A. R. ROGERS

2757. **Determination of amidopyrine in Pyrabutol-Spofa.** J. Blažek (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 576–578.—The existing methods for the determination of amidopyrine in the presence of phenylbutazone were compared and because of their inaccuracy, lack of specificity and other shortcomings, a new method is proposed. *Procedure*—Mix the injection (1 ml containing ≃ 150 mg of amidopyrine) with H_2O (10 ml) and 12·5% HCl (1 ml) and filter into a Kjeldahl apparatus. Wash the filter with hot H_2O, add 12·5% NaOH soln. (1 ml), 5% $KMnO_4$ soln. (25 ml) and boil. Then add 50% NaOH soln. (20 ml) and steam-distil the dimethylamine thus set free into a flask containing 0·1 *N* H_2SO_4 (25 ml) for 10 or 15 min. Titrate the excess of H_2SO_4 with 0·1 *N* NaOH, with a mixed indicator (methyl red - methylene blue). When analysing tablets, the sample must be dissolved in hot water. The average error is ± 2·5%. J. VOLKE

2758. **Application of mixed indicators to the control of drugs. II. A new mixed indicator for the determination of amidopyrine.** M. Zahradníček and V. Součková (Dept. of Pharm. Chem., School of Pharm., Brno, Czechoslovakia). *Českosl. Farm.*, 1958, **7** (10), 587–589.—A new indicator for the titration of amidopyrine with 0·1 *N* H_2SO_4 is proposed, namely 1 pt. of methyl orange (0·1% aq. soln.), 4 pt. of indigo carmine (0·1% aq. soln.), 2 pt. of 2:6-dinitrophenol (0·1% in 70% ethanol). For 30 ml of the titrated soln. 0·4 ml of the indicator is used. The colour change from green to violet shows a grey intermediate shade at the end-point. The average error is lower than with methyl orange.

J. VOLKE

2759. **Volumetric determination of some two-component medicinal preparations in non-aqueous media.** T. Jasiński, K. Marcinkowska and K. Węcławska (Inst. of Pharm. Chem., Gdańsk, Poland). *Acta Polon. Pharm.*, 1957, **15** (4), 261–266.—The quant. composition of some two-component mixtures of drugs, with one basic and one acid component, was determined. The basic

component (amidopyrine or phenazone) is titrated in acetic acid soln. with $HClO_4$, with methyl violet as indicator. The acid component (barbituric acid derivative, salicylic acid or 8-hydroxyquinoline-5-sulphonic acid) is titrated in pyridine soln. with a soln. of Na methoxide in benzene - methanol, with thymol blue as indicator. CHEM. ABSTR.

2760. **Ion exchangers in pharmaceutical analysis. XI. The determination of ethyl 1:2:5-trimethyl-4-phenylpiperidine-4-carboxylate hydrochloride (Promedol) and 4-*m*-hydroxyphenyl-1-methyl-4-propionylpiperidine hydrochloride (ketobemidone).** J. Vacek and L. Tyrolová (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 564–566.—Promedol (**I**) is determined by ion-exchange chromatography on Amberlite IRA-400 combined with an acidimetric titration. The u.v. spectrum of **I** was measured. A maximum at 257 mμ ($\epsilon = 42$) is suitable for quant. analysis. Ketobemidone (**II**) is more firmly bound on Amberlite IRA-400 and elution can be achieved only with *N* HCl. Thus a separation of **II** from **I** is possible. **II** is determined colorimetrically after reaction with diazotised sulphanilic acid. J. VOLKE

2761. **Determination of pyrazinamide.** J. Blažek and Z. Stejskal (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 578–580.—Pyrazinamide is hydrolysed with NaOH soln. and the NH_3 set free is determined. J. VOLKE

2762. **Assay of hexachlorophane and bithionol [2:2′-thiodi-(4:6-dichlorophenol)] in solid and liquid soaps, emulsions and dusting powders.** H. J. van der Pol (N. V. Koninklijke Pharm. Fabrieken v/h Brocades-Stheeman en Pharmacia, Meppel, Netherlands). *Pharm. Weekbl.*, 1958, **93** (20), 881–886 (in English).—The spectrophotometric method of Childs and Parks (*cf. Anal. Abstr.*, 1956, **3**, 3183) has been modified. An accuracy of ± 2% is claimed. *Procedure*—Dissolve the sample (containing 15 mg of disinfectant) in methanol, dilute to 50 ml and filter if necessary. Dilute one 5-ml aliquot to 50 ml with 0·3 *N* Na acetate in methanol and another 5 ml to 50 ml with 0·3 *N* acetic acid in methanol containing 0·15% of 4 *N* HCl. Measure the difference in the extinctions of the two soln. at 312 mμ (for hexachlorophane) or at 328 mμ (for bithionol). A. R. ROGERS

2763. **Determination of sulphatolamide (Marbadal C) alone and in Supronal.** V. Špinková and J. Černý (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 591–593.—In sulphatolamide [the =CS group reacts with $AgNO_3$ yielding a ppt. of Ag_2S; the excess of $AgNO_3$ is determined by back-titration with NH_4SCN. In Supronal tablets the argentimetric titration gives only the sulphatolamide, but titration with $NaNO_2$ gives the sulphamerazine present also. J. VOLKE

2764. **Polarographic determination of Prontosil soluble and sulphasalazine.** M. Laštovková and A. Vacková (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 570–572.—4-Hydroxy-4′ - (pyrid - 2 - ylsulphamoyl)azobenzene - 3 - carboxylic acid (sulphasalazine) is determined polarographically in a Britton - Robinson buffer pH 9·91. The height of the wave ($E_{\frac{1}{2}} \simeq -0{\cdot}6$ V) is linearly proportional to the concn. in the range 5 to 60 mg per 100 ml. Prontosil soluble is determined in a Britton - Robinson buffer pH 7·95. The 2-electron wave depends linearly on the concn. of Prontosil soluble over the range 5 to 60 mg per 100 ml. J. VOLKE

2765. **Analytical evaluation of ambazone (Iversal).** V. Špinková (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 572–575.—Ambazone (**I**) gives both cathodic and anodic waves at the dropping mercury electrode. Owing to its low solubility in acidic and neutral media, 0·2 *N* NaOH is proposed as a suitable solvent. *Procedure*—Powder the tablets, dissolve a weighed amount (2 g) in warm 0·2 *N* NaOH, and make up to 50 ml with the same soln. As soon as the ppt. has settled, pipette 2·5 ml of the clear supernatant liquid and make up to 10 ml with H_2O. Remove the O with a stream of N and record the polarographic wave. Evaluate with the aid of a calibration curve. J. VOLKE

2766. **Titrations in non-aqueous media. II. Determination of new peroral antidiabetics.** J. Kráčmarová and J. Kráčmar (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 566–569.—N-Butyl-N′-toluene-*p*-sulphonylurea (tolbutamide) (**I**) and N-*p*-aminobenzenesulphonyl-N′-butylurea (carbutamide) (**II**) can be determined by titration in anhyd. acetone or pyridine with visual or potentiometric control. *Procedure for* **I**—Dissolve the sample containing 50 to 150 mg of **I** in anhyd. acetone (10 ml) or pyridine and titrate with 0·1 *N* Na methoxide to phenolphthalein. In a mixture of benzene and methanol (2:1), thymol blue can be used as indicator. *Procedure for* **II**—If **II** is to be determined as an acid, proceed in the same way as for **I**. For a determination as a base, dissolve the sample of **II** in glacial acetic acid (10 ml) or anhyd. acetone and titrate with 0·1 *N* $HClO_4$, with crystal violet as indicator. The average error is ± 1% for the drug, or ± 2% for tablets. Approx. the same accuracy was obtained with potentiometric control (with two antimony electrodes). J. VOLKE

2767. **Potentiometric titrations of drugs with a blocked aromatic amino group. III. Titration of acetarsol as the pure substance and in commercially produced preparations.** J. Blažek (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1958, **7** (10), 589–590.—*Procedure*—To the sample (250 mg) add dil. HCl (30 ml) and boil under reflux for 30 min. Transfer the soln. into a beaker with the help of conc. HCl (40 ml), cool to ≃ 15° and titrate with 0·1 *M* $NaNO_2$ with the use of platinum and carbon electrodes. At the end-point the deflection of the galvanometer becomes constant. The average error is ± 0·1% for the pure substance, but higher with tablets and injection solutions. J. VOLKE

See also Abstracts—**2268**, Determination of procaine and amethocaine. **2715**, Determination of heparin. **2738**, Determination of pepsin. **2815**, Paper chromatography in toxicological investigations.

Food

Foods and food additives, beverages, edible oils and fats, vitamins.

2768. **Food analysis—techniques, interpretation and legal aspects.** D. Pearson (Nat. Coll. Food Technol., London). *Lab. Practice.*—The following

series of review papers has been published. **I. Introduction,** 1957, **6**, 646–648; **II; III. The British Food Laws,** 1957, **6**, 704–706; 1958, **7**, 25–26; **IV. The quality control chemist in the food industry,** 1958, **7**, 92–94; **V. The reporting of results,** 1958, **7**, 156–159; **VI. The determination of moisture, water and total solids,** 1958, **7**, 584–587; **VII. The determination of protein, ash and related constituents,** 1958, **7**, 652–655; **VIII. The determination of crude fibre and fat,** 1958, **7**, 715–718; **IX. The determination of preservatives,** 1959, **8**, 21–24; **X. Trace elements in food,** 1959, **8**, 55–57, 91–95.

2769. **Use of the Karl Fischer method for the determination of water in some products of the food industry.** L. Mináriková and F. Koromzay (Res. Inst. Food Ind., Bratislava). *Průmysl Potravin*, 1958, **9** (10), 538–541.—The Karl Fischer method can be used for the determination of H_2O content in maize, maize starch and wheat flour. *Procedure*—To 1 g of the homogenised sample add abs. methanol (25 ml) and extract for 3 min. (starch), or for 8 min. (flour) or for 18 min. (maize) with occasional shaking. Titrate 5 ml of the extract with the Karl Fischer reagent. J. ZÝKA

2770. **Determination of colouring matter in pickled meat.** K. Möhler (Dtsch. Forschungsanstalt für Lebensmittelchem., Munich, Germany). *Z. LebensmittUntersuch.*, 1958, **108** (1), 20–28.—The colouring effect of $NaNO_3$ on sausage meat is assessed by the spectrophotometric determination of the nitrosomyochromogen extracted by aq. acetone, and of the metmyochromogen extracted by acetone plus aq. HCl. The meat, after homogenisation with aq. NaCl of known concn. and adjustment to pH 5, is treated at 50° for 1 hr. with the required amount of $NaNO_3$, with or without ascorbic acid or other additives. After heating to 75° and cooling, the extractions are carried out (with exclusion of light) on separate portions by stirring with the respective solvents. The extinction value of the neutral filtered extract is carried out immediately at 540 mμ (E_{540}), and that of the acid extract, after standing for 1 hr., at 640 mμ (E_{640}). The percentage production of pickling coloration, or "percentage reddening," is calculated from the formula $(E_{540} \times 100)/(E_{640} \times 2{\cdot}5)$.

P. S. ARUP

2771. **Determination of the freezing-point depression of milk (Hortvet method).** British Standards Inst. (2 Park St., London). B.S. 3095:1959, 26 pp.—Apparatus and procedure are specified. The calculation of the result in terms of the percentage by weight of added water is described, together with methods of correction of the observed temp. readings of the Hortvet thermometer, either by reference to the N.P.L. certificate or from a calibration by means of sucrose soln.

R. E. ESSERY

2772. **Spectrochemical determination of strontium-to-calcium ratio in food, milk, cream, blood, faeces and urine of cows.** G. V. Shalimoff, J. G. Conway and A. E. Pitzer (Radiation Lab., Univ. California, Berkeley). *Appl. Spectroscopy*, 1958, **12** (4), 120–122.—A knowledge of elementary Sr to Ca ratios allows correlation with existing radioactive ^{90}Sr to Ca ratios to give the more significant ratio of ^{90}Sr to total Sr. Samples are first ashed or loaded directly on to the anode of a d.c. carbon arc. The electrode is first impregnated with NaCl, which enhances the line intensities of Sr and Ca and buffers the varying sodium content of the samples. The ratio is determined over the range 1×10^{-4} to 5×10^{-2}, with an average deviation of ± 12%.

P. T. BEALE

2773. **Isolation and identification of acidic and neutral carbonyl compounds in different varieties of cheese.** E. W. Bassett and W. J. Harper (Ohio State Univ., Columbus, U.S.A.). *J. Dairy Sci.*, 1958, **41** (9), 1206–1217.—Neutral and acid carbonyl compounds from four varieties of cheese are isolated as 2:4-dinitrophenylhydrazones. The identity of individual compounds is established by paper chromatography of the derivatives in comparison with known compounds, by light-absorption properties and, with β-keto acids, by chromatography of the neutral compounds resulting from decarboxylation. The keto acids and neutral carbonyl compounds found in different cheese varieties are listed. W. H. C. SHAW

2774. **Volatile fatty acid in soup spice.** K. Kožich and V. Mareček (Res. Inst. for Fats and Oils, Prague). *Průmysl Potravin*, 1958, **9** (10), 535–538.—A modification of the Pelshenke method (*cf. Brot. u. Gebäck*, 1955, 53) is described. Fatty acids separated by distillation were extracted with butanol or ether, separated chromatographically with the use of the system butanol - aq. NH_3 as solvent, and detected with bromocresol green (0·25% soln.). J. ZÝKA

2775. **Phenolic acids in coffee.** C. Lentner and F. E. Deatherage (The Univ., Columbus, Ohio, U.S.A.). *Chem. & Ind.*, 1958, (41), 1331–1332.—Partition chromatography on silica gel of hot aq. extracts of coffee (green or roasted), followed by paper chromatography of the band of *iso*chlorogenic acid (**I**) with $CHCl_3$ - acetic acid - H_2O (2:1:1) as solvent system, yielded **I**, two esters of ferulic acid and an ester of *p*-coumaric acid. These three hydroxycinnamic esters were identified by elution from the paper with 80% ethanol, followed by alkaline hydrolysis and paper chromatography of the hydrolysate (*cf.* Reichl, *Mikrochim. Acta*, 1956, 955; Cartwright and Roberts, *Chem. & Ind.*, 1955, 230); confirmation was obtained from the u.v. absorption spectra. Good resolution of chlorogenic acid, "compound 510" (an ester of caffeoylquinic acid) and neochlorogenic acid was obtained by two-directional paper chromatography with $CHCl_3$ - *sec.*-amyl alcohol - acetic acid - H_2O (4:3:2:4) as the solvent system for the first direction and with 2% acetic acid for the second direction. Trace amounts of caffeic acid were found, but neither free ferulic acid nor *p*-coumaric acid. W. J. BAKER

2776. **Significance of hop tannins, and a new colorimetric method for their determination.** M. Kotrlá-Hapalová and J. Soudek. *Kvasný Průmysl*, 1958, No. 1; *Brauwissenschaft*, 1958, **11** (10), 231.—Four methods for the determination of the tannins in hops are compared; preference is given to the method of de Clerck *et al.* (*cf. Bull. Ass. Éc. Brass. Louvain*, 1947, **43**, 68) which depends on the visual measurement of the coloration given in aq. soln. at pH 10 with $FeCl_3$. With the use of a spectrophotometer, the results are accurately reproducible. The relation between concn. and the extinction value is linear for the range 25 to 150 mg of tannin per litre. The intensity of the coloration given by spelt tannins is 2·4 times that given by hop tannins.

P. S. ARUP

2777. **Colorimetric semi-micro determination of phosphorus in edible oils.** E. Becker and L. Krull (Hauptlab. der Margarine-Union A.-G., Hamburg-Bahrenfeld, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (6), 447–449.—The amount of phosphorus due to the remaining traces of phosphatides is a good indication of the degree of refinement of edible oils, but sensitive methods are necessary for its determination. A small sample is calcined with MgO and the ash is dissolved in dil. H_2SO_4 and then treated with a special molybdate reagent containing hydrazine sulphate. After heating on a water bath, a blue coloration develops which is determined at 700 mμ. The standard curve is prepared by the use of Na_2HPO_4 soln. The sensitivity is 5 mg of P_2O_5 per kg of oil in a sample of 1·3 g.

A. TESSLER

2778. **Analysis of monoglycerides and of free glycerol.** E. Becker and L. Krull (Hauptlab. der Margarine-Union A.-G., Hamburg-Bahrenfeld, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (6), 449–452.—Two methods for the determination of monoglycerides are discussed; both are based on the quant. reduction of H_5IO_6 by monoglycerides. The resulting HIO_3, together with the excess of H_5IO_6, is determined according to Pohle and Mehlenbacher's method (*cf. J. Amer. Oil Chem. Soc.*, 1950, **27**, 54), iodimetrically in acid soln., whereas Kruty *et al.* (*cf. Anal. Abstr.*, 1955, **2**, 1676) employ a neutral medium which leaves the HIO_3 unchanged so that only the excess of H_5IO_6 need be determined. The advantages of the latter method are pointed out, namely, greater accuracy, wider limits in the quantity of the sample and the possibility of the determination of the glycerol content without a preliminary separation. Only the α-monoglycerides can be determined by these methods. Any β-isomer that may be present must first be transformed into the α-form by treating it with a small amount of H_5IO_6 which acts as a catalyst. Several commercial samples were examined and were found to contain the whole of their monoglyceride content in the α-form, undoubtedly as a result of self-isomerisation during storage. Treatment with the catalyst is therefore required only for fresh material. Attempts were made to ascertain the diglyceride content by calculation from the hydroxyl values, but quite small errors in the determination of the monoglycerides and especially of the glycerol make the calculation unreliable. It is therefore recommended that, for this method to be of any value, the monoglycerides and the glycerol should be determined, with the greatest possible accuracy, separately, by removing the glycerol by washing.

T. TESSLER

2779. **Differential thermal analysis. III. Melting curves of oils and fats.** J. Hannewijk and A. J. Haighton (Unilever Lab., Vlaardingen, Holland). *J. Amer. Oil Chem. Soc.*, 1958, **35** (9), 457–461.—Differential thermal analysis has been applied to the study of the behaviour on melting of fats and oils. Curves obtained are of a shape dependent on pre-treatment of the fats; they indicate the degree of tempering of the fat, and also the formation of mixed crystal types.

G. R. WHALLEY

2780. **Refractometry of fats. VIII. Polyphase refractometric determination of the aniline point.** H. P. Kaufmann, J. G. Thieme and R. Scholz (Dtsch. Inst. f. Fettforschung, Münster, Westf.). *Fette, Seif., Anstrichmitt.*, 1958, **60** (10), 957–963.—The aniline point may be determined to a precision of ± 8 in the fourth decimal place by use of an Abbé refractometer for observing the appearance of the meniscus at the critical mixing temperature (appearance of two lines in place of one) at a cooling rate of 0·3° per min. The application of the method to several fats, particularly lard, and to the products of their solvent fractionation, is illustrated.

J. L. PROSSER

2781. **Microphotometric evaluation of chromatographic spots. Application to fatty acid mixtures.** E. Vioque, A. Vioque and M. Pilar de la Maza (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1958, **9** (4), 168–175.—The fatty acids are separated on paper impregnated with a petroleum solvent (boiling-range 170° to 230°); aq. acetic acid is used as mobile phase, and the acids are revealed by conversion into copper salts and treatment with dithio-oxamide. A negative of reduced dimensions is obtained from the chromatogram illuminated by transmitted light. The photometric areas are then measured by a registering photometer and used for the calculation of the fatty acid composition. Typical results for mixtures of C_{12}, C_{14}, C_{16} and C_{18} saturated acids are given. Erroneous results obtained by simple measurement of the areas of the spots on the chromatogram are indicated.

L. A. O'NEILL

2782. **Paper-chromatographic separation of higher fatty acids with continuous change of solvent concentration during the separation.** V. Palo, V. Koman and Z. Hrabě (Inst. Tech. Microbiol. and Biochem., High-School of Chem. Technol., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1958, **12** (9), 525–532.—The apparatus previously described (Koman and Palo, *Ibid.*, 1958, **12**, 513) has been applied to the separation of stearic, oleic, palmitic, myristic, lauric and other fatty acids from hydrolysed oils, and R_F values have been determined. The separation can be carried out with 5% benzene soln. of fatty acids (50 to 200 μg) on filter-paper impregnated with a 10% soln. of liquid paraffin in benzene. Acetic acid is used as solvent. The dried chromatograms are immersed in $CuSO_4$ soln. (20 ml of a satd. soln. of $CuSO_4$ mixed with 240 ml of H_2O), then washed, and the copper salts of the separated fatty acids are detected with 7·5% $K_4Fe(CN)_6$ soln.

J. ZÝKA

2783. **Nomograms for calculating and testing the Morton and Stubbs correction in the spectrophotometric assay of vitamin A.** G. Pancrazio and V. Duse (Res. Lab., ORMA, Ist. Terapeut. Romano, Rome). *Analyst*, 1958, **83**, 579–584.—Two nomograms, one for vitamin-A alcohol in *iso*propyl alcohol and the other for vitamin-A acetate in abs. ethanol, are given for the rapid application of the Morton and Stubbs correction, without numerical calculation, to spectrophotometric measurements. Application of the Morton and Stubbs correction sometimes leads to erroneous results. By means of two subsidiary measurements at 318 and 330 mμ, and the use of these nomograms, the validity of the application of the correction to the measurements can be tested.

A. O. JONES

2784. **Quantitative spectrophotometric determination of the components of a mixture by differential measurement at the isosbestic point. Determination of vitamins B_1, B_2, B_6 and nicotinamide in admixture.** R. Hloch and K. Capek (Bundesanstalt f. Chem-Pharm. Untersuch., Vienna, Austria). *Sci. Pharm.*, 1958, **26** (3), 168–183.—Mixtures

whose components exhibit a pH-dependent absorption, and with it the formation of isosbestic points, can be quant. resolved by differential spectrophotometry. Two soln. of the mixture at different pH values are measured against one another at the isosbestic wavelength of one of the components. The extinction of this compound is therefore cancelled and the observed extinction is due to other components of the mixture. By further measurement at the isosbestic points of the other components a series of extinction values are obtained which enable the composition of the mixture to be calculated. The method is illustrated by the quant. determination of vitamins B_1, B_2, B_6 and nicotinamide in admixture. The absorption spectra of these compounds were compared at various pH values and the isosbestic points and extinction coeff. determined for the invididual vitamins. Vitamin B_2 was measured directly at 450 mμ; vitamins B_2 plus B_6, B_1 plus nicotinamide, and B_1 plus B_2 were measured at 324, 267 and 254·7 mμ, respectively. By equating the extinction coeff. and these measurements, the concn. of the individual vitamins were found. Errors for the individual components were generally $\gtrsim \pm 3\%$ in the concn. range of 1 to 100 mg. G. P. Cook

2785. **Ferricyanometric determination of ascorbic acid.** B. R. Sant (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Chemist Analyst*, 1958, **47** (3), 65.—To a known aliquot of ascorbic acid soln. add 10 to 15 ml of 15% Zn acetate soln., 2 to 3 drops of 1% KI soln. and 1 ml of starch indicator. Titrate slowly with 0·1 *N* $K_3Fe(CN)_6$, the end-point being shown by the sudden appearance of a blue colour due to the liberation of iodine from the KI by the excess of $K_3Fe(CN)_6$. The zinc salt precipitates the $Fe(CN)_6^{4-}$ as it is formed, and maintains the pH in the region of 6. Results for amounts of ascorbic acid between 1·90 and 95·00 mg agreed well with those by the iodate-iodide method. Quantities < 2 mg can be determined with more dilute $K_3Fe(CN)_6$ soln.

R. E. Essery

2786. **Potentiometric and amperometric titrations of ascorbic acid.** S. M. Deshpande and R. Natarajan (Dept. of Chem., Coll. of Sci., Hindu Univ., Benares). *J. Amer. Pharm. Ass., Sci. Ed.*, 1958, **47** (9), 633–635.—Ascorbic acid can be determined by titration with aq. $KMnO_4$ in the presence of KI to avoid oxidation of the dehydroascorbic acid produced. With potentiometric detection of the end-point, quantities of < 1 mg can be determined with an error of $< \pm 1{\cdot}5\%$. The end-point may also be detected with the dropping mercury electrode at an applied potential of $-1{\cdot}0$ V *vs.* the S.C.E., but the sensitivity is less. *Procedure*—Mix the sample with 2 *N* H_2SO_4 (2 ml) and 0·5% KI soln. (1 ml), dilute with H_2O to 50 ml and titrate with 0·001 *N* $KMnO_4$.

A. R. Rogers

See also Abstracts—**2649**, Chromatographic separation of erucic acid. **2711**, Determination of riboflavine in urine. **2753**, Assay of panthenol.

Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

2787. **Fractional sublimation technique for separating atmospheric pollutants.** J. F. Thomas, E. N. Sanborn, Mitsugi Mukai and B. D. Tebbens (Sanit. Engng Res. Lab., Univ. of Calif., Berkeley). *Anal. Chem.*, 1958, **30** (12), 1954–1958.—An apparatus is described for quant. separation of condensed polynuclear aromatic hydrocarbons, in particular carcinogens, by fractional sublimation. When applied to atmospheric samples, several fractionations are necessary to remove a resinous component. The rate of sublimation is a function of temp. and pressure; the linear temp. gradient in the apparatus is adjustable and pressures of 5·0 to 0·01 mm (Hg) are used. Fractions are obtained by cutting the fractionating tube into sections.

P. D. Parr-Richard

2788. **Polarographic determination of sulphur dioxide in the atmosphere.** E. Zvîncă-Selegean, L. Cariadi and N. Racoveanu. *Rev. Chim., Bucharest*, 1958, **9** (1), 39–44.—From a comparison of various methods, it is claimed that the most sensitive is the colorimetric one with a lower limit of 0·1 μg, followed by the nephelometric (2 μg), polarographic and conductimetric (10 μg) and the iodimetric (14 μg). The upper limits are 10 μg for colorimetric, 15 to 20 μg for nephelometric, judged visually, or 50 to 60 μg with a Pulfrich turbidimeter. For determinations between 1 and 15 μg, results from the colorimetric, nephelometric and polarographic methods are in good agreement. Only the nephelometric and polarographic methods can be considered satisfactory for specificity. *Procedure*—The sample is aspirated into 10 ml of 0·1 *N* NaOH, and amounts from 0·1 to 2 ml are pipetted into the cell, and diluted to 5 ml with HCl (0·1 *N*) plus 2 drops of methyl red. The polarograms have $E_{\frac{1}{2}}$ for SO_3 lying between $-0{\cdot}2$ and $0{\cdot}4$ V, and must be obtained at exactly the same temp. as that used for the standard curves. Concn. of up to 0·1 mg of Cl, 0·003 g of NH_3 and 0·02 mg of H_2S per litre do not appreciably affect the results. H. Sher

2789. **Detection of heterosubstituted aromatic derivatives and determination of aromatics in the air.** E. Sawicki, T. W. Stanley and T. R. Hauser (Taft San. Engng Center, U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio). *Chemist Analyst*, 1958, **47** (3), 69, 77.—Certain aromatic compounds yield diarylmethane dyes with piperonylidene chloride in trifluoroacetic acid. The air (1000 cu. metres) is passed through a glass-fibre filter, which is then extracted with benzene in a Soxhlet apparatus for 8 hr., the benzene evaporated at 60°, and the residue weighed and dissolved in 10 ml of $CHCl_3$. For the qual. test, 1 drop of this soln. is added to 1 micro drop of reagent (5% of piperonaldehyde and 6·8% of PCl_5 in $CHCl_3$; stable for 3 hr. at room temp.) and 10 drops of trifluoroacetic acid in a test-tube and shaken gently. A red, violet, purple, blue or green colour indicates the presence of aromatics. The test is given by aromatic and hetero-aromatic compounds that have their highest electron density at an aromatic carbon atom, and are less basic than benzene under the conditions of the test. Aliphatics, benzene, quinones, and electronegatively substituted compounds, such as acetophenone and nitrochrysene, do not react. For the quant. procedure, 1 ml of the soln. is mixed with 1 ml of reagent, made up to 10 ml with trifluoroacetic acid, well mixed, and allowed to stand for 5 min. The absorption spectrum is then determined from 400 to 800 mμ against a $CHCl_3$ blank. For each wavelength max., a "*K* value" (defined as the specific absorption coeff. of organic matter from 1000 cu. metres of air per 100 ml of treated soln.), which is proportional to the amount of compound present

in the sample, is given by $(100\ E/M)(W_1/W_a)$, where E is the absorbance in a 1-cm cell, W_1 is the total weight in mg of the benzene extract from M cu. metres of air, and W_a is the wt. in mg of benzene extract actually analysed. The colours produced, and corresponding wavelength max., are listed for 18 compounds. R. E. ESSERY

2790. **Simple thermal-conductivity meter for gas analysis, with special reference to fumigation problems.** H. K. Heseltine, J. D. Pearson and H. Wainman (Pest Infestation Lab., D.S.I.R., Slough, England). *Chem. & Ind.*, 1958, (40), 1287–1288.—Measurement, under field conditions, of the concn. of fumigant in air has been achieved with the portable meter illustrated. To obtain results in 2 to 3 min. with a sample vol. of 200 ml, and to have a full-scale deflection corresponding to a level of 40 to 80 mg of methyl bromide per litre (1 to 2%) with an accuracy of $\pm$ 0·5 mg per litre, the thermal-conductivity method of Phillips and Bulger (U.S.D.A. Publ. E851) for the measurement of methyl bromide in air has been adapted. Prototype instruments of different sensitivities have been constructed, and measurements at the 1 mg per litre level are possible. The circuit diagram is shown and further modifications are discussed.
E. G. CUMMINS

2791. **Photometric gas analyser for determining toxic concentrations of oxides of nitrogen in the air.** M. T. Borok (Design Bureau of Analytical Apparatus Manufacture). *Zavod. Lab.*, 1958, **24** (9), 1128–1134.—The apparatus is described. G. S. SMITH

2792. **Determination of micro amounts of copper, lead and zinc in natural waters and soil extracts without using cyanide.** A. D. Miller and R. I. Libina (Lensovet Leningrad Technol. Inst.). *Zhur. Anal. Khim.*, 1958, **13** (6), 664–667.—Two methods have been developed—(*i*) for quant. isolation of Pb from a mixture of Zn and Pb dithizones (after separating Cu in the usual way) by treatment with thiosulphate at pH $\simeq$ 5·5 to 6·0, and (*ii*) for separate determination of Cu, Zn and Pb by re-extraction of Zn and Pb diethyldithiocarbamates, treatment with HCl soln. of different concn. and titration with dithizone. (*i*) To 500 ml of an aq. sample soln. add 2 ml of 25% ascorbic acid soln. or 5 ml of satd. NH_4NO_3 soln. (extracted with dithizone) and adjust the pH to 8·0 to 8·5 with aq. NH_3. Extract Cu, Zn and Pb with 5 ml of dithizone in CCl_4, then shake the combined extracts for 2 min. with two 5-ml portions of 0·10 to 0·15 N HCl, and re-extract the CCl_4 layer with metal-free water; the aq. phase contains Pb and Zn, whereas Cu remains in the organic layer, and can be determined photometrically. Neutralise the aq. soln. containing Pb and Zn with aq. NH_3 to phenol red and titrate with dithizone to slight excess. Shake the soln. successively with dil. aq. NH_3 (1:300), to remove the excess of dithizone, with metal-free water, and with 5 ml of 10% $Na_2S_2O_3.5H_2O$ soln. (previously shaken with dithizone, and of pH 5·5 to 6·0). Make the extract alkaline to phenol red and determine Pb by "extraction titration" with dithizone in CCl_4. After separation of Pb, determine Zn immediately in the CCl_4 layer by re-extracting it with 0·01 to 0·02 N HCl, neutralising to phenol red with aq. NH_3, and "extraction titration." For an acid soln. of sample, take an aliquot so that the total metal content of Pb, Zn and Cu will be in the range 10 to 25 μg. Almost neutralise the soln. with aq. NH_3, dilute with an approx. equal volume of 0·10 to 0·20 N HCl, add 2 ml of 25% ascorbic acid soln. and determine Cu by titration with dithizone. Determine Zn and Pb as described above. (*ii*) To an aq. sample soln. (500 ml) add 10 ml of 5 N $CaCl_2$ (previously shaken with dithizone), 2 ml of 5% Na diethyldithiocarbamate soln., and 10 ml per litre of satd. ammonium citrate soln. and adjust the pH to 8·5 to 9·0 (phenol red or thymol blue). Add 15 ml of CCl_4 and shake for 5 min., then transfer the CCl_4 layer into a separating-funnel and extract with 0·1 N HCl (4 $\times$ 5 ml) to remove Zn and determine it as in (*i*). Wash the CCl_4, now containing only Cu and Pb, with metal-free water and shake with 3 N HCl (2 $\times$ 5 ml) to remove Pb. Neutralise the extract containing Pb to phenol red with aq. NH_3 and determine Pb as in (*i*). Determine the Cu photometrically immediately after removing Pb.
W. ROUBO

2793. **A single solution method for the determination of soluble phosphate in sea water.** J. Murphy and J. P. Riley. *J. Mar. Biol. Ass. U.K.*, 1958, **37**, 9–14.—It has been found that a mixture of H_2SO_4, ammonium molybdate and ascorbic acid can be used as a single soln. reagent for the determination of phosphate in sea water. Development of the molybdenum-blue colour is complete in 24 hr. at room temp. and in 30 min. at 60°, and the colour is stable for at least 3 days. Beer's law is obeyed up to a concn. of at least 500 μg of phosphate-phosphorus per litre. The salt error is approx. 4% with sea water of chlorinity 19·3 parts per thousand. The interference caused by arsenate and silicate is negligible at the concn. at which these ions occur in sea water. WAT. POLLUT. ABSTR.

2794. **Rapid photometric determination of fluoride in water. Use of sodium 2-(*p*-sulphophenylazo)-1:8 - dihydroxynaphthalene - 3:6 - disulphonate [SPADNS] - zirconium lake.** E. Bellack and P. J. Schouboe (Div. of Dental Public Health, U.S. Public Health Service, Washington, D.C.). *Anal. Chem.*, 1958, **30** (12), 2032–2034.—Rapid determination of F^- in water is possible with a mixed reagent containing SPADNS and zirconyl chloride in 0·7 N HCl. The extinction is read at 570 mμ; Beer's law is obeyed for samples containing up to 1·40 mg of F^- per litre, but sample and standards must be tested at the same temp. Many common ions do not interfere, but free Cl should be removed.
P. D. PARR-RICHARD

2795. **Determination of small amounts of bromine and iodine in hot springs by the micro-diffusion method.** Akito Koga (Inst. for Balneotherapy, Kyushu Univ., Beppu, Oita-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79** (9), 1026–1029.—Conway's method was applied to hot-spring water ($<$ 6 mg of Br and $<$ 3 mg of iodine per litre). The unit used had an inner diameter of 8 cm. The absorption of iodine ($<$ 30 μg) and Br ($<$ 300 μg) is complete within 24 hr. when 20% KI soln. (0·5 ml) is used. The water sample (10 to 100 ml) is made alkaline, evaporated to $<$ 10 ml, neutralised with N H_2SO_4 (phenolphthalein), mixed with N H_2SO_4 (1 ml) and $K_2Cr_2O_7$ (2 g) and kept overnight in the dark in the unit containing 20% KI soln. (0·5 ml). The KI soln. is mixed with 1% starch soln. (0·8 ml) and water (1·0 ml) and submitted to colorimetry. For the determination of Br, 60% H_2SO_4 (5 ml) is added to the sample soln. used for the determination of iodine, the Br is absorbed in fresh 20% KI soln. (0·5 ml) overnight and titrated with 0·005 N $Na_2S_2O_3$. K. SAITO

2796. **Rapid method for the determination of carboxylic acids in phenolic effluents.** C. Mrázová and V. Mráz (Stalinovy Závody, Záluží, Czechoslovakia). *Chem. Průmysl*, 1958, **8** (8), 415–417.—Potentiometric titration in pyridine medium with a soln. of KOH in methanol yields good results. *Procedure*—To 2 ml of the sample, containing 2 to 15 g of carboxylic acids per litre, add pyridine (30 ml) and titrate with 0·1 *N* KOH in methanol, with potentiometric control. Aq. NH_3 soln., phenolic compounds, CO_2 and H_2S do not interfere.
J. ZÝKA

2797. **Micro-determination of 2:3-dichloro-1:4-naphthaquinone (Phygon) in water.** J. E. Newell, R. J. Mazaika and W. J. Cook (Naugatuck Chemical, Div. of U.S. Rubber Co., Conn.). *J. Agric. Food Chem.*, 1958, **6** (9), 669–671.—Micro amounts of the algicide and fungicide Phygon (**I**) in water are determined by filtering off insol. matter, adding NaCl to the filtrate, acidifying it with H_3PO_4, and distilling off **I**. **I** is then extracted from the distillate with $CHCl_3$, the $CHCl_3$ is evaporated off, and **I** is determined by measurement of absorption at 253·8, 259, 283·5 and 299 mμ, a base-line technique being used to reduce background error introduced by other u.v.-absorbing materials. The method is applicable in the range 8 to 250 parts per 10^9, with an average recovery of 86%, the deficit being attributable to slight hydrolysis, and to incomplete recovery in the distillation.
M. D. ANDERSON

See also Abstract—**2642**, Determination of carbohydrates in sea water.

Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

2798. **Methods for the determination of boron and their application to fertilisers with special reference to potentiometric titration.** K. Lang (Inst. of Agric. Testing and Res., Bonn, Germany). *Z. anal. Chem.*, 1958, **163** (4), 241–250.—Five methods are described and compared and their use in the determination of boron in nine fertilisers is studied. Taylor's potentiometric method (*Brit. Abstr. C*, 1950, 376) has been simplified to give quick and accurate results. The removal of CO_2 and PO_4^{3-} before titration is unnecessary. This method is also applicable to coloured fertilisers without prior extraction. Sixty to seventy analyses can be carried out in 8 hr.
B. B. BAUMINGER

2799. **Determination of fat in fish meal by refractometry.** H. Treiber (Zentral-Lab. der "Nordsee" Dtsch. Hochseefischerei A.-G., Bremerhaven, Germany). *Fette, Seif., Anstrichmitt.*, 1958, **60** (6), 488–490.—The method is based on a suggestion by Dreosti and van Merwe ("Progr. Rep. No. 18. Fishing Ind. Res. Inst., Cape Town"). 1-Chloronaphthalene was used as fat solvent. The results were about 0·2% higher than the figures obtained by the usual Soxhlet method as improved by Twisselmann, and these higher figures are thought to be more reliable.
A. TESSLER

2800. **Analysis of insecticides and fungicides.** D. A. Sousa and N. F. Almeida (Inst. Biologico, São Paulo). *Inst. Biol. São Paulo, Brasil*, 1957 [1958], 93 pp.—This is a collection of recommended methods, which are described fully, for the quant. analysis of some 40 common insecticides and fungicides, and for the examination of inert compounding materials, oils and emulsions. (44 references.)
S.C.I. ABSTR.

2801. **Quantitative infra-red analysis of pesticides in the solid state.** H. Susi and H. E. Rector (Rohm & Haas Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 1933–1935.—The potassium bromide pellet technique has been used for the study of four pesticides [Mn ethylenebis(dithiocarbamate) hydrate, *pp'*-dichlorobenzil and mixtures of 1:1-bis-(4-chlorophenyl)trichloroethanol and 1:1-bis-(4-chlorophenyl)trichloroethylene] [?], and the results suggest that quant. analysis is possible, provided that samples of known composition are studied beforehand and uniform grinding and mixing procedures are used. No internal standard is used.
K. A. PROCTOR

2802. **Chemical studies on insecticides. IX. Infra-red absorption spectra of phosphorus acid esters.** J. A. A. Ketelaar and H. R. Gersmann (Lab. Gen. Inorg. Chem., Univ., Amsterdam). *Rec. Trav. Chim. Pays-Bas*, 1959, **78** (3), 190–195.—The i.r. absorption spectra of 30 phosphorus acid esters have been measured and recorded.
N. E.

2803. **Parathion and *p*-nitrophenol in biological material.** A. T. H. van der Meulen (Rijksinst. Volksgezondh., Utrecht, Netherlands). *Chem. Weekbl.*, 1958, **54** (29), 380–384.—Results are presented of a critical investigation of the errors in the determination of parathion (**I**), *p*-nitrophenol (**II**) and their mixture. Steam-distillation causes a loss of 10 to 20% of **I** and about the same proportion of **II** distils over. **I** can be determined in the distillate without interference by **II**. Detailed methods are given for determining **I** in blood serum, stomach contents and urine.
P. RENTENAAR

2804. **Extension of the residue methods for 1:2-dihydro-3:6-pyridazinedione (maleic hydrazide) and N-1-naphthylphthalamic acid (Alanap).** J. R. Lane, D. K. Gullstrom and J. E. Newell (Naugatuck Chemical, Div. of U.S. Rubber Co., Conn.). *J. Agric. Food Chem.*, 1958, **6** (9), 671–674.—Wood's method (*cf. Anal. Abstr.*, 1954, **1**, 1125) for determining maleic hydrazide by alkaline hydrolysis, and measurement after reaction of the hydrazine with *p*-dimethylaminobenzaldehyde, is modified in several ways for residues on tobacco, including addition of $FeCl_2$ to the tobacco before distillation with NaOH, to ensure quant. recovery of hydrazine. The extinction is read at 430, 460 and 490 mμ, and the result is obtained by a base-line calculation. The previous method for determining N-1-naphthylphthalamic acid residues by steam-distillation of 1-naphthylamine from basic soln., and reaction with diazotised sulphanilic acid, is modified for use on smaller residues by increase of sample size, extraction of 1-naphthylamine from the distillate with *n*-hexane to eliminate interferences, and extraction from hexane into aq. acid. The colour is measured at 480, 534 and 600 mμ, and results are obtained by a base-line calculation.
M. D. ANDERSON

2805. **Determination of tetrachloro-*p*-benzoquinone (Spergon) [chloranil] residues on food crops.** J. R. Lane (Naugatuck Chemical, Div. of U.S. Rubber Co., Conn.). *J. Agric. Food Chem.*, 1958, **6** (9), 667–669.—The reactive chlorine atoms of the fungicide chloranil (**I**) tend to combine with the

plant constituents. **I** can be determined by dissolving it from the plant surfaces with benzene, and using the quinone groups to oxidise diphenyl-*p*-phenylenediamine to a blue Wurster salt. This is extracted from the benzene with aq. acetic acid - HCl, the extinction is measured at 700 mμ, and the content of **I** is read from a standard curve. The recovery of additions of 0·1 to 0·9 p.p.m. was 72 to 115%. M. D. ANDERSON

2806. **Determination of small amounts of triphenyltin acetate on plants.** S. Gorbach and R. Bock (Anal. Lab., Farbwerke Hoechst A.-G., Germany). *Z. anal. Chem.*, 1958, **163** (6), 429–432.—Triphenyltin acetate on fresh leaves is removed by repeated rinsing with $CHCl_3$ to which is added a few ml of 0·1 *N* NaOH. The $CHCl_3$ extracts are collected and shaken with an alkaline tartrate soln. to remove other compounds of Sn. After evaporation of the $CHCl_3$ and destruction of the organic matter, Sn is determined polarographically. Possible interferences of Pb and HCl can be eliminated. B. B. BAUMINGER

See also Abstracts—**2489**, Determination of Mg in soil extracts. **2493**, Determination of Sr in soil ash. **2792**, Determination of metals in soil extracts. **2797**, Determination of 2:3-dichloro-1:4-naphthaquinone (Phygon) in water.

5.—GENERAL TECHNIQUE AND APPARATUS

General

2807. **A nomographic calculator for organic analysis.** M. Neeman and H. Tabor (Res. Council Israel, Jerusalem). *Bull. Res. Council Israel, A*, 1957, **7** (1), 41.—The simple calculator shown and described can be used to read off directly the theoretical element-percentage composition from the known empirical formula of any reaction product, or vice versa. There are scales for any combination of elements and radicals. A rapid and accurate check can thus be made of assumed formulae against the analytical values for an unknown substance, *e.g.*, in organic elementary micro-analysis. W. J. BAKER

2808. **A technique for small-scale crystallisations.** M. Martin-Smith (The University, Glasgow). *Lab. Practice*, 1958, **7** (10), 572–574.—The apparatus, modified from earlier designs (*cf.* Cockburn, *Canad. J. Chem.*, 1951, **29**, 715, and Craig and Post, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 413), and the centrifuge technique employed are described and illustrated. Advantages of the method are discussed. O. M. WHITTON

2809. **Recording burette.** D. A. Miller (Sci. Service Lab., Univ. Sub P.O., London, Ontario, Canada). *Anal. Chem.*, 1958, **30** (12), 2067–2068.—In this method of operating a recording burette a platinum-wire probe is lowered mechanically until it makes electrical contact with the meniscus of the titrant, which must be an electrolyte. As the meniscus drops, the contact is broken, and an electromechanical device is actuated and further lowers the probe to re-establish contact. A recording device is linked with the movement of the probe. K. A. PROCTOR

2810. **Chemical method for calibration of Warburg manometers.** C. R. Scott and W. B. Dandliker (Dept. of Biochem., Univ. of Washington, Seattle, U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2074.—The calibration procedure described is based on gas evolution from a quant. chemical reaction and affords an accuracy comparable with that of the laborious mercury method (Dixon, "Manometric Methods," 2nd Ed., Macmillan, New York, 1943). K. A. PROCTOR

2811. **Rapid evaporation of solutions in test-tubes.** C. E. Pierce and T. D. Perrine (U.S. Dept. of Health, Educ. and Welfare, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2069–2071.—Modifications to an Evapo-mix (a distillation apparatus) to protect the sample from contamination are described. Other modifications have been made for convenience in use. K. A. PROCTOR

2812. **A micro-fractional vacuum sublimation - distillation apparatus.** T. H. Bates (Chem. Div., A.E.R.E., Harwell, England). *Chem. & Ind.*, 1958, (41), 1319–1320.—In the arrangement described and illustrated, a horizontal glass tube (50 cm × 2 cm) has its inner and outer surfaces insulated with asbestos paper, whilst a spiral of nichrome wire is wound round the outer surface to produce a uniform temp. gradient along the tube. The sample (10 to 100 mg in a small test-tube) is inserted into another glass tube (55 cm × 1 cm) with a closed end, which is then evacuated to a pressure of $< 1\ \mu$ of mercury, sealed off and placed inside the wider tube. The temp. is raised slowly (by increasing the voltage at 10-min. intervals in 10-V steps) to that required, *e.g.*, 170° for separating a mixture of diphenyl and the three terphenyl isomers, and is kept constant for $\simeq$ 1 hr. The inner tube is then removed and cooled in a horizontal position. The four fractions can be extracted by cutting the tube, and their weights obtained by weighing the sections before and after removal of the contents. W. J. BAKER

See also Abstract—**2790**, Thermal-conductivity meter for gas analysis.

Chromatography, ion exchange, electrophoresis

2813. **The *T*-effect: a method for increasing resolution in some systems in which substances traverse a medium at different rates.** M. M. Tuckerman, R. A. Osteryoung and F. C. Nachod (Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chim. Acta*, 1958, **19** (3), 249–251 (in English).—The separation of substances by techniques in which differences in rates of traverse of a medium are exploited (chromatography, ion exchange, etc.) may be improved by using two media in tandem. A mathematical treatment is given of the conditions necessary for maximum resolution with this principle (*T*-effect). T. R. ANDREW

2814. **Chromatography of molten salts on a glass-powder column.** M. M. Benarie (Scientific Dept., Min. of Defense, Tel-Aviv, Israel). *Science*, 1958, **128**, 1008.—The apparatus consists of a Pyrex-glass column, 8 mm internal diam., 20 cm long, filled with Pyrex-glass powder (100 to 140 mesh) placed in a vertical oven. A eutectic mixture of LiCl and KCl (m.p. 352°) containing 0·1 to 1% of the chlorides of heavy metals showed separation into

zones comparing favourably with solution chromatography. Elution with the eutectic mixture could be made with the same ease as with the aq. solution process. H. F. W. KIRKPATRICK

2815. **Experience with paper chromatography in toxicological investigations.** J. Schmidlin-Mészáros (Chem. Lab., Gerichtl.-Med. Inst., Univ. Zürich). *Chimia*, 1958, **12** (9), 275–281.—The paper chromatography of the barbiturates, α-ethyl-α-phenylglutarimide (glutethimide), the ureas, pyrazolones and some alkaloids is discussed. The reliability and legal value of the chromatographic technique is emphasised and its correct use alongside the more classical techniques is described with some examples. E. KAWERAU

2816. **Separation of inorganic isomeric *cis* - *trans* compounds by paper chromatography and the effect of configuration on R_F values.** G. Stefanović and T. Janjić (Chem. Inst., Fac. Sci., Belgrade, Yugoslavia). *Anal. Chim. Acta*, 1958, **19** (5), 488–492.—Inorganic *cis* - *trans* isomers have been examined in a number of developing solvent mixtures. Ten Co complexes, one Pt complex and one Cr complex were examined. Seven solvent mixtures were studied, containing acetone as the major component, together with H_2O, HCl, HNO_3, HBr or KI. Except in the case of the Cr complex, separation was obtained with all seven mixtures, *cis* compounds having higher R_F values than the corresponding *trans* isomers. The Cr complex was separated by using a solvent mixture containing diethyl ether, ethanol and H_2O (18:3:1). This mixture did not resolve any of the other compounds. T. R. ANDREW

2817. **Simple rapid method for circular paper chromatography.** A. J. Philippu (Lab. of Physiol., Univ. of Athens, Greece). *Nature*, 1958, **182**, 1159.—A circle (1·5 cm in diam.) is drawn in the centre of a filter-paper 26 cm in diam. Cuts are made along diagonals to form triangular wicks, and these are bent downwards to dip into the solvent contained in a small vessel placed on a support in a glass desiccator 25 cm in diam. The spot is applied to the periphery of the circle between the cuts, and the desiccator is closed. Development proceeds as a circle. H. F. W. KIRKPATRICK

2818. **Direct-print photographic paper for rapid analysis of paper chromatograms containing ultraviolet-absorbing materials.** F. M. Ganis (Univ. of Rochester Sch. of Med. and Dentistry, Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2068–2069.—The method described produces an immediate print of a chromatogram without the necessity or delay of chemical processing. It has been used in the analysis of chromatograms containing u.-v.-absorbing materials, particularly steroids, of the order of 5 μg or more per sq. cm of paper. K. A. PROCTOR

2819. **Efficiency of columns for vapour-phase chromatography.** P. Chovin (Lab. Municipal de Paris). *Bull. Soc. Chim. France*, 1958, **7**, 905–910.—The effects of the several factors, column size, nature of carrier gas, adsorbent, stationary phase, temp., and pressure differential, are discussed and expressions derived for evaluating the results of altering a given set of conditions. T. R. ANDREW

2820. **Main principles of planning gas-chromatographic equipment and methods of determination.** J. Toth (Oil Res. Lab., Nagykanizsa, Hungary). *Magyar Kém. Foly.*, 1958, **64** (10), 382–391.—Based on the adsorption theory of gas chromatography, the principles of planning equipment suitable for the analysis of a given natural gas are detailed. The possibilities and errors of measuring techniques are compared and discussed. G. SZABO

2821. **A multiple-fraction collector for gas chromatography.** I. M. Napier and H. J. Rodda (Univ. of Adelaide, S. Australia). *Chem. & Ind.*, 1958, (41), 1319.—The design and operation of a multiple-fraction collector for columns run at high temp. and reduced pressure are described. The receivers are plain U-tubes fitted at each end with B7 cones and are cooled in acetone - "dry ice." W. J. BAKER

2822. **Preparation and properties of kieselguhr used as a support in gas chromatography.** J. Brodský and J. Zmítko (Res. Inst. of Synth. Rubber, Gottwaldov, Czechoslovakia). *Chem. Listy*, 1958, **52** (10), 2012–2013.—Powdered kieselguhr is mixed with a small vol. of H_2O, dried at 110°, heated to 500° in a furnace and then ground (0·2 to 0·4 mm or 0·4 to 0·5 mm). The suitability of the product has been tested with good results on various stationary phases (*e.g.*, dioctyl phthalate, dibutyl phthalate, dioctyl adipate and dimethylformamide). J. ZÝKA

2823. **Gas - liquid chromatography of hydroxyl and amino compounds. Production of symmetrical peaks.** H. S. Knight (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1958, **30** (12), 2030–2032.—The fundamental causes of unsymmetrical peaks in gas chromatography have been investigated. The peak symmetry of polar substances can be improved by adding a similar polar material continuously with the carrier gas and by operating the column at the proper temp. K. A. PROCTOR

2824. **Removal of heavy metals from ion-exchange resins used for trace metal analysis.** R. A. Edge (Div. of Chem. Services, Dept. of Agric., Capetown, S. Africa). *Chemist Analyst*, 1958, **47** (3), 72.—The procedure of Johnson and Polhill (*Analyst*, 1957, **82**, 238) is advocated. For cation exchangers, condition the resin by stirring it on a boiling-water bath for 1 hr. with *M* NaOH. Decant the supernatant soln. and stir the resin on the bath for 15 min. with 0·2 *M* EDTA brought to pH 8 to 10 with NaOH soln. Decant, repeating the treatment with EDTA if the supernatant liquid is highly coloured. Wash the resin thoroughly with water. Heat on the bath for 1 hr., with stirring, with 4 or 5 separate portions of 5 *M* HCl. Wash free from acid with de-ionised water. Air-dry, and store in a polyethylene bottle. For anion exchangers, treat the resin overnight with 2 *M* HCl. Transfer to an exchange column, and cycle successively with 1 *M*, 0·01 *M*, and 1 *M* HCl. R. E. ESSERY

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	A
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic.	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline	cryst.
crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	% (v/v)
per cent. (wt. in vol.)	% (w/v)
per cent. (wt. in wt.)	% (w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_F
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, $Fe^{\cdot\cdot+}$, etc., for cations and by Cl^-, SO_4^{2-} PO_4^{3-}, etc., for anions.

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ANALYTICAL ABSTRACTS

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